

Manuals of Pure and Applied Chemistry

General Editor

R. M. CAVEN, D.Sc (Lond), F.R.C.

COMPLEX SALTS

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BY

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PREFACE

This book has been written more especially for students reading for Final and Honours Degrees. It differs from the German works on Complex Salts in that it discusses cognate questions connected with the study of the subject, such as methods of investigation, molecular asymmetry, chemical analysis, &c.

The book is not intended to be an encyclopædia-- the intention has been rather to write a book on chemistry than to compile a collection of facts.

In preparing the book, the author has made free use of the following works, and wishes here to acknowledge his obligation to the respective authors: *New Ideas on Inorganic Chemistry*, by Alfred Werner, translated by A. Hedley; *Anorganische Komplex Salze*, by E. Weinland; *Principles of Symmetry*, by F. M. Jaeger (Cambridge University Press); and *Chemical Analysis*, by Stieglitz.

The author wishes to express his gratitude to Professor Findlay for his valuable advice and criticism, to his colleague, Dr. J. E. Humphries, who read the manuscript and proofs, and made many helpful suggestions, and to Professor Caven, editor of the series, who has suggested many alterations and additions which have increased the value of the book.

W. THOMAS.

THE CHEMICAL DEPARTMENT,
THE UNIVERSITY, ABERDEEN.
March, 1924.

EDITOR'S NOTE

After many years of neglect chemistry is at length being recognized in this country as one of the most important factors of modern life. Evidence of this recognition is shown by the increased notice which the subject is receiving in the public press, and by the large numbers of books that are being issued on various aspects of the science. It is now clearly seen that chemical science contributes to the health, comfort, luxury, and intellectual life of the modern citizen. It is a difficult task, nevertheless, to bring the latest achievements of chemistry within the reach of minds untutored in its first principles, though this task should be attempted by those best qualified to perform it.

The purpose of the present series of manuals, however, is to provide for those who have a working knowledge of chemistry—for graduates in science and medicine, for workers in various branches of applied chemistry, for teachers, and for all who have an intellectual interest in the science for its own sake—readable accounts of modern developments written by experts in the subjects with which they deal.

This volume is concerned with a subject which is of great theoretical interest because the chemical compounds with which it deals lie within the borderland of chemical combination, in a region which the earlier theories of valency, simple, stereotyped, and sufficient for most purposes, could not reach.

As these complex compounds accumulated they were labelled "molecular", and so dismissed; though chemists must have been aware that some day an attempt would have to be made to elucidate their nature.

After lesser lights came the brilliant illumination from the works and theories of Alfred Werner. Werner not only enriched greatly

our knowledge of complex compounds, but provided and substantiated a theory of their structure which we are glad to acknowledge to-day. Of particular importance was Werner's demonstration of the stereochemistry of the ammines and related compounds, culminating in the actual isolation of optically active isomers having in their molecules metallic atoms as nuclei. This achievement, it will be universally admitted, stands out as one of the most notable peaks in the "Oberland" of inorganic chemistry.

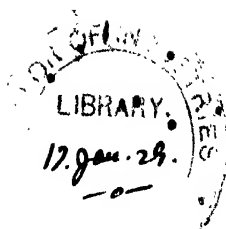
With the advent of electronic theories of valency interest in complex inorganic compounds has been enhanced. We desire to have a mental picture of these compounds; we wish to know not only how all the atoms in their molecules are related to one another in space, but also what are the electrical forces which hold these atoms in their several spheres.

This picture is coming into focus, though it is not yet sharply defined. We hope to gain in time a clear conception not only of the planetary system of each atom, but of the stellar system of the molecular universe of the most complex chemical compound.

Dr. Thomas, himself a worker in this field, has provided in this volume a synoptic view of our present knowledge of this branch of inorganic chemistry.

R. M. CAVEN.

ROYAL TECHNICAL COLLEGE, GLASGOW,
March, 1924.



CONTENTS

CHAPTER I

	Page
VALENCY AND THE CO-ORDINATION THEORY - - - - -	1
Recent Theories of Valency - - - - -	4
Werner's Theory - - - - -	5

CHAPTER II

METHODS OF DETECTING THE FORMATION OF COMPLEX SALTS - - -	11
Molecular Weight Determinations - - - - -	12
Electrical Conductivity - - - - -	12
Solubility Method - - - - -	15
Distribution Coefficient Method - - - - -	17
Ionic Migration Method - - - - -	18
Electromotive Force Measurements - - - - -	19
Phase-rule Method - - - - -	20
Colour - - - - -	20

CHAPTER III

TYPES OF INORGANIC COMPLEX SALTS - - - - -	21
Compounds with Co-ordination Number Six - - - - -	21
The Hexammine Group - - - - -	21
Hexammine-Cobaltic Chloride - - - - -	21
Hydrates - - - - -	25
The Monacido-Pentammine Group - - - - -	26
The Diacido-Tetrammine Group - - - - -	30
The Triacido-Triammine Group - - - - -	32
The Tetracido-Diammine Group - - - - -	33
The Pentacido-Monammine Group - - - - -	34
The Hexacido Group - - - - -	35

CHAPTER IV

SPATIAL ARRANGEMENT AND ISOMERISM - - - - -	37
Determination of the Configuration - - - - -	39

CONTENTS

	Page
Other Types of Isomerism - - - - -	43
Structure Isomerism - - - - -	43
Co-ordination Isomerism - - - - -	44
Ionization Isomerism - - - - -	44
Hydration Isomerism - - - - -	45
Polymerism - - - - -	46
CHAPTER V	
MOLECULAR ASYMMETRY AND OPTICAL ACTIVITY - - - - -	47
CHAPTER VI	
METHODS OF RESOLUTION - - - - -	57
Separation by Spontaneous Crystallization - - - - -	57
Separation by Combination with an Active Molecule - - - - -	60
Separation by Living Organisms - - - - -	63
CHAPTER VII	
CHARACTERISTICS OF OPTICALLY ACTIVE COMPLEX SALTS - - - - -	64
Anomalous Rotation - - - - -	64
Rotatory Power and Constitution - - - - -	68
Optical Activity and Configuration - - - - -	69
Racemization - - - - -	72
Optical Activity and Crystalline Form - - - - -	74
CHAPTER VIII	
COMPOUNDS WITH CO-ORDINATION NUMBER FOUR - - - - -	76
<i>Co-ordination Number Equal to Four</i> - - - - -	76
The Tetrammine Group - - - - -	76
Monacido-Triammine Group - - - - -	77
Diacido-Diammine Group - - - - -	78
Triacido-Monammine Group - - - - -	78
Tetracido Group - - - - -	79
<i>Configuration and Isomerism</i> - - - - -	80
CHAPTER IX	
STABILITY OF INORGANIC COMPLEX SALTS - - - - -	83
<i>Stability of Complex Salts in Solution</i> - - - - -	87
Double Salts—Complex Salts - - - - -	87
The Precipitation Method - - - - -	88
The Electromotive Force Method - - - - -	89

CONTENTS

xi

Page

CHAPTER X

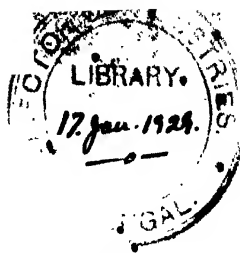
INORGANIC COMPLEX SALTS AND CHEMICAL ANALYSIS	92
<i>Application to Qualitative Analysis</i>	92
Chlorides, Bromides, and Iodides	92
Copper and Cadmium	93
Cobalt and Nickel	94
<i>Application to Quantitative Analysis</i>	95
The Analysis of a Complex Salt	96

CHAPTER XI

RÉSUMÉ	90
Co-ordination Number Six	99
Co-ordination Number Four	100
Valency	100
Basic Salts	102
Poly-acids	103
Water of Crystallization	104
Factors affecting Stability of Complex Salts	104
The Neutral Component	104
The Ionic Component	106
Earlier Views on the Constitution of Complex Salts	108

CHAPTER XII

PREPARATION AND RESOLUTION OF INORGANIC COMPLEX SALTS	111
Potassium Ferrocyanide	111
Potassium Ferricyanide	112
Sodium Nitroprusside	113
Sodium Cobalti-nitrite	114
Chloro-pentammine-Cobaltic Chloride	114
Nitro-pentammine-Cobaltic Chloride	115
Nitrito-pentammine-Cobaltic Chloride	115
Preparation of Erdmann's Salt	116
Estimation of Cobalt in Erdmann's Salt	116
Preparation and Resolution of Potassium Cobalti-oxalate	117
Resolution of Triethylenediamine-Chromic Iodide	118
NAME INDEX	119
SUBJECT INDEX	121



COMPLEX SALTS

CHAPTER I

Valency and the Co-ordination Theory

The introduction of quantitative methods into chemistry by Lavoisier and others led chemists to investigate the mass relationship of the elements in the different chemical compounds. The laws of constant and multiple proportions, Dalton's atomic theory, and Avogadro's hypothesis, were the early fruits of the researches which were inspired by the new methods. These laws and the theories derived from them summarize the quantitative relationship between the elements and the compounds they form, but they attempt no explanation of chemical affinity; and while the laws have remained unchanged during the last century, the views as to the nature of the combination of the elements have undergone much variation.

In 1812 Berzelius¹ enunciated his dualistic theory, which regards the affinity between atoms and molecules as being electrical in origin, and as due to the excess of one kind of electricity over the other in a polar system. Berzelius² later joined forces with Liebig³ in developing the theory of radicles, which followed the realization of the phenomenon of isomerism. The existence of isomeric compounds was explained by Berzelius by assuming different arrangements of the atoms and radicles in the molecule, an idea which has remained, and, moreover, has been further developed, despite the fact that the dualistic theory was opposed by Dumas⁴ and later by Gerhardt⁵ in their theory of types. The ideas of these latter chemists were gradu-

¹ *Schweigger's Journ.*, 6, 119.

² Wöhler and Liebig, *Ann.*, 3, 249 (1832).

³ *Ann. Chim. Phys.*, 72, 184 (1839).

⁴ *Jahresber.*, 11, 44 (1832).

⁵ *Ann. Chim. Phys.*, 33, 179, 259.

COMPLEX SALTS

ally superseded by the ideas of Frankland,¹ Kekulé,² and Couper.³ At this period the dualistic theory of Berzelius fell into disuse and was replaced by the unitary idea of valency, according to which the affinity between elements to form compounds is all of one type.

The chief contention between chemists for the remainder of the nineteenth century centred around the ideas of fixed and variable valency. Frankland in his classical paper in 1852 considered variable valency as probable; Kekulé, on the other hand, regarded valency as fixed, and a definite property of an element as constant as its atomic weight. The application of Kekulé's theory of constant valency received great support from and led to extensive researches in the realm of organic chemistry. Difficulties were, however, experienced in the formulation of inorganic compounds on the basis of constant valency of the elements. This led to such formulæ as $\text{Cl}_2\text{Fe}-\text{FeCl}_2$ for ferrous chloride in order to keep the valency of iron equal to three as in ferric chloride. Further, phosphorus pentachloride and ammonium chloride were regarded as molecular compounds, PCl_3Cl_2 and NH_3HCl , this method of formulation being supported by the dissociation of the compounds. Later work, however, showed that such formulæ were untenable, so that the theory of variable valency was accepted, and efforts were made to explain it.

Kolbe⁴ gave to each element a maximum valency, the saturation of which made further combination impossible; he assumed, however, that compounds could exist in which the maximum valency was not brought into play. Mendeléef, accepting this view, stated that this maximum valency was exhibited in the highest oxides (leaving out of consideration the peroxides). Van't Hoff⁵ regarded the external form and shape of the atom as the cause of valency. An atom in motion continuously changes its external form, and, therefore, according to this theory, its valency changes. Since an increase in temperature increases atomic motion, one would expect as a result a decrease in valency; this is supported by the fact that at higher temperatures molecules generally dissociate to give simpler molecules, e.g. H_2F_2 , N_2O_4 , PCl_5 , NH_4Cl , &c. Elements are frequently monatomic at higher temperatures, e.g. iodine; this means, according to van't Hoff, that the motion of the atom has increased to such an extent that its valency is zero.

Abegg has advanced another theory, which includes that of

¹ *Phil. Trans.* (1852). ² *Ann.*, 106, 129 (1858). ³ *Phil. Mag.*, 16, 104 (1858).

⁴ *Lehrbuch d. anorg. Chem.*, Vol. I (1856). ⁵ *Ausrichten über die anorg. Chem.*, 1880.

Kolbe, that each element has a maximum valency, and that before combination occurs these valencies are of equal strength. When, however, combination takes place, the saturation of one valency of an element weakens the others the extent of weakening depending on the number of its valencies which are active, and on the nature of the element or group with which it has entered into combination. Abegg thus regards unused valency as being latent and of varying strength. Nef, on the other hand, assumes that these unused valencies saturate one another, so that ammonia and phosphorus trichloride would be formulated $<\text{NH}_3$ and $<\text{PCl}_3$ respectively.

The valency of an atom in the first place depends on the atom with which it combines. Many elements show a higher valency for oxygen than for the other elements; thus manganese gives an oxide Mn_2O_7 , where the atom manganese is septavalent; towards chlorine, however, the maximum valency of manganese is four, as in MnCl_4 . Iron forms an oxide FeO_3 containing a sexavalent iron atom, whereas the highest chloride of iron is FeCl_3 , with the iron atom trivalent. The elements also show a high valency towards fluorine. Thus sulphur is sexavalent towards oxygen and fluorine (cf. SO_3 and SF_6), but its maximum valency towards chlorine is four as given in the compound SCl_4 .

The valency of an element, again, depends on external conditions, as has already been shown above in the discussion of van't Hoff's theory of variable valency. The dissociation of carbon dioxide and sulphur trioxide at high temperatures may be further cited as showing that the valency generally decreases with increasing temperature.

Valency thus depends on various factors; i.e. the capacity of an atom to combine with other atoms is determined by the conditions of the experiment. This term valency or capacity for combination must not be confused with the term affinity, which expresses the intensity of combination. The relationship between the capacity and the intensity of combination was expressed by Blomstrand¹ in 1869. He stated that the valency of an atom was inversely proportional to its affinity; i.e. those elements which are very electropositive or electronegative have the lowest saturation capacity. Since the affinity of an atom of one element for atoms of the different elements is a varying quantity, variable valency is a result of Blomstrand's generalization.

The ideas of directed valency were developed by van't Hoff²

¹ *Chemie d. Jetztzeit*, 1869.

² *Voorstel tot Uitbreiding der Structuur-Formules in de Ruimte* (1874).

and Le Bel,¹ who formulated a space configuration for carbon compounds, and were thus able to explain the existence of isomers. This idea of directed valency failed, however, in some important particulars, viz. ethylenic and acetylenic linkages, molecular transformations, and racemization of optically active compounds.

Abegg² considered that each atom possesses two kinds of valency, which he called normal and contra valency. These are of opposite polarity; the normal valency is the stronger and is the usual characteristic valency of the element. Metals combine with the non-metals to form stable compounds; their normal valency is thus positive, and vice versa for the non-metals. Abegg states that the sum of the normal and contra valencies of an element is always equal to eight. The relationship between the values of these valencies and the position of the element in the periodic classification is shown in the following table.

Groups	1	2	3	4	5	6	7
Normal valency	+1	+2	+3	+4	-3	-2	-1
Contra do.	-7	-6	-5	-4	+5	+6	+7

Contra valency is stronger in the non-metals than in the metals. This is shown by the fact that non-metallic elements are generally polyatomic, whilst the vaporized metals are monatomic. Again, the contra valency increases in a group with the atomic weight; e.g. fluorine forms no oxide, whereas iodine forms at least two oxides.

Recent Theories of Valency.—The theory of Berzelius, which was advanced in 1812, was electrochemical. Then followed entirely different theories advanced by Dumas, Gerhardt, and others. Modern theories are again electrochemical and are based on the modern conception of the atom, which is regarded as being constituted of a positive nucleus surrounded by negative electricity.

Sir J. J. Thomson³ bases his views of valency on his conception of atomic structure. He regards the atom as consisting of a positive charge surrounded by an arrangement of electrons which are fixed on the surfaces of spheres with the positive charge as centre. Eight electrons are assumed to be the maximum number on the surface of one sphere, and Thomson regards the stable arrangement of these

¹ *Bull. de la Soc. Chim.*, **22**, 337 (1874).

² Abegg and Böllander, *Zeit. anorg. Chem.*, **20**, 453 (1899); Abegg, *Zeit. anorg. Chem.*, **39**, 330 (1904).

³ *Phil. Mag.*, **41**, 521 (1921).

VALENCY AND THE CO-ORDINATION THEORY

eight electrons as being at the corners of a twisted cube. If the central charge is nine, eight electrons will form a spherical shell concentric with the central charge, and one electron will find a position of stable equilibrium outside this sphere. This resembles an atom with one electron. If the nuclear charge is ten, the outer shell will contain two electrons, and so on. There will thus be a periodicity of the number of electrons in the outer shell, and since the chemical properties of the elements are supposed to depend on the outer shell, the elements will show periodicity in accordance with the periodic classification. Sodium has one electron in the outer shell; it may thus combine with an element by giving it this electron, i.e. it has a positive valency equal to one. On the other hand it may take up seven electrons in order to complete its shell; this would mean a negative valency of seven. Thomson shows that this valency probably remains inactive. Fluorine has an outer shell containing seven electrons; it can take up one electron to form a stable shell, i.e. it has a negative valency equal to one. Thomson assumes the formation of molecules as being due to the electrons acting as couplings.

Lewis¹ and Langmuir² have advanced similar ideas, but differ from Thomson in assuming a cubic lattice instead of the twisted cube for the position of the eight electrons. Their atomic models and the related theory of valency have achieved great success in explaining the number and variety of chemical compounds, but they have not attempted to explain physical properties, e.g. spectra, which require dynamical models as advanced by Rutherford and Bohr.

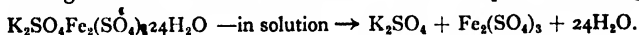
Werner's Theory. Difficulties were experienced in the application of the existing theories of valency to molecules of hydrated salts, double salts, and complex salts. In the case of copper sulphate crystals, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, four of the water molecules were driven off at 105°C ., whereas a temperature of over 200°C . was necessary to expel the fifth molecule. From this the conclusion was drawn that four of the molecules of water were held by a crystallographic force, but that the fifth entered more intimately into the constitution of the molecule. In dealing with the hydrates in general, a series can be drawn up where one passes from compounds in which water is very lightly held to compounds with stronger combination, and finally to cases in which the water is very strongly held. The following may serve to illustrate this:



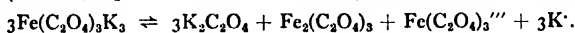
¹ *J.A.C.S.*, 38, 762 (1916).

² *J.A.C.S.*, 41, 868 (1919).

Since, therefore, the difference between these compounds is only a difference of degree, this points to the probability that the mode of linkage is the same in all (see later). Further, it can be shown that the transition from double to complex salts is a gradual one. The alums on being dissolved in water dissociate into their component salts, e.g.



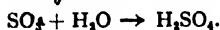
One assumes, therefore, that the reason for the existence of these double salts is not chemical but crystallographic, depending on the various ways of packing of the atoms and molecules in the crystals. Potassium ferrioxalate when dissolved in water dissociates to an appreciable extent into potassium oxalate and ferric oxalate, as can be shown by analytical tests. The solution also contains the complex ion, as can be shown by the addition of a solution of a barium salt, when a green precipitate of barium ferric oxalate is formed. Hence the following equilibrium exists in an aqueous solution of this salt:



Further, potassium ferricyanide may be cited as an example of a very stable complex salt. The formulation $\text{Fe}(\text{CN})_3\text{KCN}$ does not represent the reactions of this compound, because it indicates that its aqueous solution would contain potassium, ferric, and cyanide ions. The production of a blood-red coloration, $\text{Fe}(\text{CNS})_3$, with a solution of a thiocyanate is a very delicate test for the ferric ion; but this test is not given by a solution of potassium ferricyanide, so that the concentration of the ferric ion is very low in the solution. Similarly, negative tests are obtained for the cyanide ion. Hence the dissociation of potassium ferricyanide into its components must be very slight, and the above formulation is unsatisfactory.

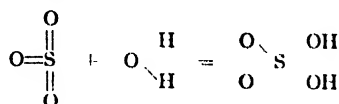
Among the various efforts that have been made to overcome this difficulty, the suggestions brought forward by Blomstrand, Jörgensen, and others proved cumbersome and unsuitable; they will be discussed in a later chapter. The first successful effort to bring law and order into the chemistry of these complex salts was made by Werner, who brought forward his "co-ordination theory", representing a new mode of formulation.

Werner calls binary compounds (oxides, halides, &c.) compounds of the first order; these simple compounds may combine together to form what he called compounds of a higher order, e.g.

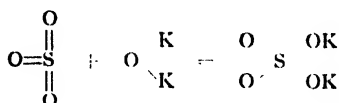


The doctrine of valency explains the formation of sulphuric acids

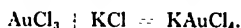
and oxyacids in general by assuming that the doubly linked oxygen atom can be transformed into two hydroxyl groups.



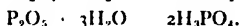
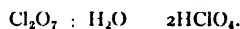
Similarly



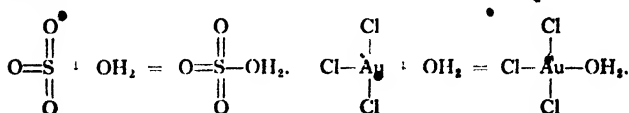
Werner claims that this mode of representation is incorrect. In the first place, this explanation depends on the bivalency of oxygen, and cannot, therefore, be applied to compounds which do not contain such plurivalent atoms attached to the central atom; yet similar compounds of a higher order are formed by the haloids, e.g.



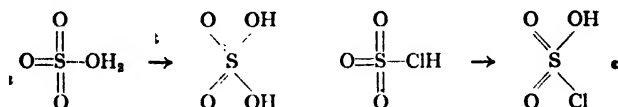
Again, the above explanation would lead one to expect the oxides richest in oxygen, such as OsO_4 and RuO_4 , to be the most suitable for the formation of hydrates, but as a matter of fact these oxides are unable to take up water. It may be stated in general that the number of water molecules taken up by an oxide is independent of the number of doubly linked oxygen atoms which it may contain. Chlorine heptoxide, for example, can take up only one molecule of water in spite of the seven double-linked oxygen atoms, whereas phosphorus pentoxide, with five such oxygen atoms, can take up three water molecules.



In the oxyacids, HClO_4 , H_2SO_4 , H_3PO_4 , HMnO_4 , &c., the maximum number of oxygen atoms seems to be four, and Werner thinks that this may explain the fact that OsO_4 and RuO_4 are unable to take up water. He assumes that the combination takes place as follows:



This formulation is in harmony with the fact that the two acids are prepared by the same method, and are similar in behaviour. If the reacting molecule contains several doubly bound atoms, then Werner admits the possibility and even the probability that the primary product will pass into a primary valency (i.e. ordinary valency, see later) compound.



The following may be cited as further examples of compounds of a higher order formed by the compounds of the first order:



The above explanation as set forth by Werner demanded a new conception of valency, and he introduced the following ideas. The atoms of elements in binary compounds are saturated, as far as their ordinary valency is concerned, but they may still possess a residue of unsaturated affinity which permits them to combine with other atoms containing similar residual affinity. Thus in the above cases Werner assumes that the S in SO_3 , Au in AuCl_3 , Pt in PtCl_4 , O in H_2O , Cl in HCl , N in NH_3 , &c., possess such a residue of unsaturated affinity, permitting them mutually to satisfy one another and form compounds of the above type. The stability of the molecular complexes formed will depend on the amount of this residual affinity—in some cases these are extremely stable. This new valency differs from the ordinary valency in that it is unable to effect the union of univalent radicles, and Werner proposed to call it Auxiliary Valency, whilst ordinary valency was called Principal Valency. Werner defines principal valencies as manifestations of affinity which permit their saturation capacities to be measured in terms of hydrogen atoms or their equivalent. Auxiliary valencies he defines as manifestations of affinity which bring about the stable union of radicles, the latter being able themselves to act as independent molecules, e.g.

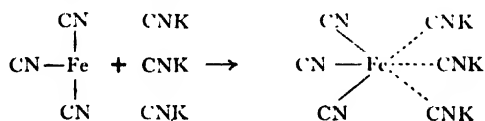
Principal valency: $\text{Cl}-$, NO_2- , $\text{Na}-$, $\text{Cu}-$, CH_3- , &c.

Auxiliary valency: $-\text{OH}_2$, $-\text{ClH}$, $-\text{NH}_3$, $-\text{SO}_3$, $-\text{PtCl}_4$, &c.

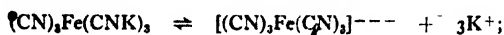
These two types of valency are very closely related, and the

saturation of the one may strengthen or weaken the other. Higher oxides which are unstable are often rendered stable by salt formation, e.g. oxides corresponding with the ferrates, the bromates, and many of the persalts. The tri- and tetra-chlorides of manganese cannot be prepared, but their double salts with alkali metals are easily obtained. The ordinary salts of trivalent cobalt are unstable, but the complex salts are stable. The weakening of ordinary valency by the auxiliary valencies is seen in the case of the complex ferric salts, which are very unstable and easily undergo reduction to the ferrous complexes.

The application of this theory to the formulation of inorganic complex salts will be made clear in the sequel, but it may be well to make a few points clear before proceeding. We will consider potassium ferricyanide, which is formed by the combination of ferric cyanide and potassium cyanide. Thus:

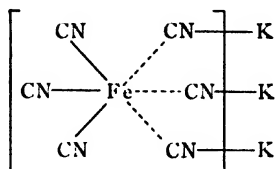


This combination is brought about by the saturation of the residual affinity of the iron atom in ferric cyanide by the residual affinity of the cyanogen groups in three molecules of potassium cyanide. In the above formulation principal valencies are represented by continuous lines, whereas auxiliary valencies are represented by broken lines. We thus have six cyanogen groups directly attached to the central iron atom, three attached by principal valency and three by auxiliary valency. Werner now states that atoms which are directly attached either by principal or auxiliary valency to another atom are in the first or undissociable zone or sphere (i.e. immediately surrounding the central atom), hence in aqueous solution these six cyanogen groups remain firmly attached to the iron atom and do not undergo ionization. The three potassium atoms, on the other hand, are in the second zone or sphere, and undergo ionization. An aqueous solution would therefore ionize according to the following equilibrium:

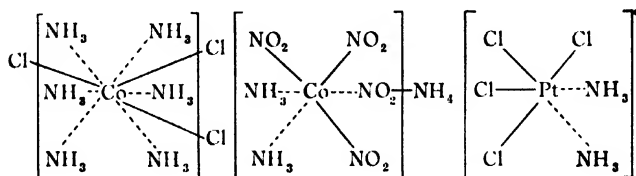


i.e. in aqueous solution we have potassium ions and also the complex ferricyanide ions. In the formulation of the salt Werner suggests

enclosing the complex ion in a square bracket and representing it thus:



It is seen that the principal valencies of three of the six cyanogen groups which are in the first zone of the iron atom are satisfied by the three potassium atoms which are found in the second zone. The following are further examples:



The part within the square bracket is generally known as the co-ordinated complex. In each of the examples cited it is seen that there are six groups in the co-ordinated complex, i.e. there are six groups in the first sphere of the central atom, and the co-ordination number is therefore said to be six. In the majority of the complex salts the co-ordination number is equal to six, but a large number of compounds are known in which it is equal to four. It is also known to possess other values; these will be considered later. The question naturally arises, has the co-ordination number any significance? Werner adopted the idea of spherical atoms and that the first sphere groups are arranged around the central atom, so that the co-ordination number signifies the number of atoms or groups which can arrange themselves in the first sphere of attraction of another atom.

CHAPTER II

Methods of Detecting the Formation of Complex Salts

Before dealing with the different types of complex salts, it will be well to discuss briefly the methods employed in their study. The methods described in this chapter are, in the main, those which have been used to determine the constitution of the compounds appearing in the sequel. It will be noted that the methods aim at determining the number and nature of the ions formed by a complex salt in aqueous solution.

The ordinary tests of qualitative analysis are tests for ions. Consider, for example, a solution of copper sulphate. The copper ion is detected by the blue colour of the solution, and by the formation of a black precipitate by hydrogen sulphide even in the presence of dilute hydrochloric acid. Similarly the presence of the sulphate ion is indicated by the precipitation of barium sulphate. If potassium cyanide is added to a solution of copper sulphate a white precipitate of cuprous cyanide is produced which dissolves in excess of potassium cyanide. From this solution a compound can be separated containing potassium, copper, and the cyanide radicle. On applying qualitative tests to a solution of this substance the presence of potassium ions is easily detected, but the solution is colourless and gives no precipitate with hydrogen sulphide. We therefore conclude that there are no copper ions present in the solution. Similarly, ordinary qualitative tests indicate the absence of cyanide ions. The presence of potassium ions, however, necessitates the presence of anions, and the conclusion is drawn that the anion is complex in nature containing copper and the cyanide radicle. Thus qualitative reactions indicate the nature of ions present in solution.

The presence of certain ions in solution can be detected by catalytic tests. Thus Bredig and Walton¹ investigated the decomposition of hydrogen peroxide by iodides, and found that the rate

¹ *Zeit. Electrochem.*, 9, 114 (1903).

of evolution of oxygen¹ was proportional to the concentration of the iodide ion. The addition of iodine to a solution of potassium iodide decreases its catalytic power, presumably by reducing the concentration of the iodide ion. This can be explained by assuming that the free iodine combines with the iodide ion to form complex I_3^- ions ($I^- + I_2 \rightarrow I_3^-$), and that the complex ions formed have no catalytic effect on the decomposition of hydrogen peroxide.

Molecular Weight Determinations.—Several methods are available for the determination of the molecular weights of substances in solution, and of these the most suitable, in the study of the inorganic complex salts, is the freezing-point method. This method is naturally carried out at low temperatures, and thus the danger of decomposition of the complex is reduced to a minimum. If w gm. of a substance when dissolved in W gm. of the solvent lowers the freezing-point of the latter by d° , the molecular weight of the solute is obtained by means of the expression

$$m = k \frac{w}{dW},$$

where k is a constant depending only on the solvent employed.

In the case of electrolytes the molecular weight in aqueous solution is found to be much smaller than the theoretical value, thus pointing to a dissociation of the substance in solution. The molecular weight as found gives the average weight of the independent particles in solution, i.e. of the undissociated molecules and the ions. Thus in the case of NaCl, which has a molecular weight of 58.5, the value found is always less than this number, and diminishes with increasing dilution to a limiting value 29.25, which is one-half of the theoretical value. This indicates that the salt in solution dissociates into two ions, i.e. that sodium chloride is a binary electrolyte. In the case of sodium sulphate the limiting value is one-third of the theoretical value, showing that the solute is a ternary electrolyte. We thus see that the number of ions given by a molecule in solution can be determined by the above method. Examples illustrating the application of this method in elucidating the structure of inorganic complex salts will be found later in this chapter.

Electrical Conductivity.—The conductance of the electric current by an aqueous solution is due to the presence of ions in solution. These ions are the carriers of the electricity, and the conductivity will depend on the number of such carriers and the speed with which they move. In comparing the conductivity of solutions

¹ $2H_2O_2 \xrightarrow{\text{in presence of } I^-} 2H_2O + O_2$.

of different solutes it is necessary to calculate the equivalent or molecular conductivities; in the case of the complex salts the latter is the more suitable.

Molecular conductivity is defined as the conductance of a solution containing one molecule of the solute between two electrodes of indefinite size and 1 cm. apart. One factor affecting the conductivity of a solution is the number of ions present, so that one would expect the molecular conductivity of sodium sulphate solution to be greater than that of sodium chloride, because the ions from a molecule of the former ($\text{Na}^+ + \text{Na}^+ + \text{SO}_4^{--}$) carry twice as much electricity as the ions from a molecule of the latter ($\text{Na}^+ + \text{Cl}^-$). If this were the only factor influencing molecular conductivity, then all binary electrolytes would have the same value, and, similarly, all ternary electrolytes, &c. This, however, is not the case because the ions move with different speeds, the faster moving ions effecting the transfer of more electricity in unit of time than the slower moving ions. Acids and bases have a much higher molecular conductivity than salts, due to the fact that the hydrogen and hydroxyl ions have a much higher mobility than the other ions, as can be seen from the following table:

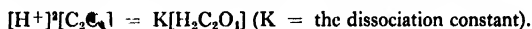
Temperature 18° C.

H = 315. OH = 172. Cl = 65.5. Na = 43.5.
K = 64. Ag = 54.3. $\frac{1}{2}\text{Cu}$ = 46.

Two or more solutions containing the same concentration of ions will have conductivities proportional to the mean mobility of their ions. Leaving out of consideration the fast-moving hydrogen and hydroxyl ions, the variations in the speeds of the ions are not very great, so that the molecular conductivities of dilute solutions are, in the main, a measure of the number of ions obtained from each molecule. This will be made clear by reference to the following table, where μ indicates the molecular conductivity, and ν the molecular dilution in litres, i.e. the number of litres of solution which contain one gramme-molecule of the solute.

	NaCl.	KClO ₃ .	AgNO ₃ .	BaCl ₂ .	MgBr ₂ .	K ₂ SO ₄ .	AlCl ₃ .	CeCl ₃ .
ν .	μ .	μ .	μ .	μ .	μ .	μ .	μ .	μ .
128	113	122	126	224	215	246	342	366
256	115	125	128	237	225	257	371	381
512	117	126	130	248	230	265	393	393
1024	118	128	131	260	235	273	413	408

The addition of a mineral acid increases the concentration of hydrogen ions in the solution. Now, oxalic acid is a comparatively weak acid, i.e. it is not very highly ionized in aqueous solution. The presence of a high concentration of hydrogen ions will therefore cause some of the oxalate ions to combine with them, as otherwise the dissociation constant of oxalic acid would be exceeded:

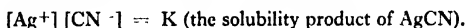


This removal of oxalate ions from solution causes more of the salt to dissolve, which explains why calcium oxalate is soluble in mineral acids. It is also seen that the addition of one of the ions already present would decrease the solubility of a salt. Thus the addition of concentrated hydrochloric acid to a saturated solution of common salt causes a precipitation of the salt.

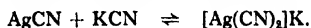
The application of the solubility method to the study of inorganic complex salts will be made clear by considering the solubility of silver cyanide. This salt is very sparingly soluble in water. If we take a saturated solution of the salt in contact with the solid, and add to the solution some potassium cyanide solution, we shall expect, from what has been said above, a decrease in the solubility of the silver salt. We have in a saturated solution of silver cyanide the following equilibria:



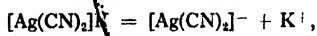
and by the application of the law of mass action



The normal effect of the addition of cyanide ions would be to cause the precipitation of the silver cyanide, i.e. to decrease the concentration of silver ions. It is found, however, that more of the silver cyanide dissolves. This, at first, seems at variance with the results obtained by the application of the law of mass action to equilibria in solution, but the disagreement is only apparent. The silver cyanide forms a complex salt with the potassium cyanide:



This complex ionizes in aqueous solution according to the following equation:



i.e. the complex does not give silver ions in solution, and in spite of the fact that on the addition of potassium cyanide more of the silver

salt goes into solution, the concentration of the silver ion actually decreases. If the process is carried out quantitatively, it is found that one gramme-molecule of silver cyanide requires one gramme-molecule of the potassium salt for complete solution—a fact which is in agreement with the above equation. Further examples of the application of the solubility method will be discussed in the sequel.

Distribution Coefficient Method.—If a substance, e.g. succinic acid, which is soluble in ether and in water is shaken up with a mixture of the two liquids, it will distribute itself between the two solvents in the ratio of its solubility in each of them.

Representing by C_1 and C_2 the concentration of succinic acid in the two solvents, the following results have been obtained:

C_1 , Water.		C_2 , Ether.		C_1/C_2 = constant.
0.024	0.0046	5.2
0.070	0.013	5.4
0.121	0.022	5.5

The above relationship holds only if the molecular weight of the solute is the same in the two solvents. The application of this method to the study of inorganic complex salts can best be illustrated by the work of Roloff,¹ who studied the reaction which occurs in aqueous solution between bromine and potassium bromide. Solutions of potassium bromide were shaken with a strong solution of bromine in carbon bisulphide, and the amount of bromine which passed into the aqueous layer was found by titration. Suppose, for example, that bromine is shaken up with a mixture of water and carbon bisulphide, it will distribute itself between the two solvents in the ratio of its solubilities in them according to the above law.

$$\frac{\text{Concentration of Br}_2 \text{ in aqueous layer}}{\text{Concentration of Br}_2 \text{ in CS}_2 \text{ layer}} = \frac{[\text{Br}_2]_{\text{aq}}}{[\text{Br}_2]_{\text{CS}_2}} = \text{constant K.}$$

If potassium bromide is now added to the aqueous layer, it will be found that bromine passes from the carbon bisulphide to the water; the above relationship must, however, still hold. Hence the bromine in the aqueous layer, over and above that required by the above equation, must be used up to form different molecular aggregates. The bromine interacts with the bromide to form a tribromide:



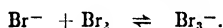
or



¹ *Zeit. Phys. Chem.*, 13, 341 (1894).

Suppose that on shaking water with a solution of bromine in carbon bisulphide, D gramme-molecules per litre pass into the aqueous layer, and that on the addition of the bromide in such amount that its concentration is A gramme-molecules per litre, then B gramme-molecules of bromine pass into the aqueous layer. $B - D$ gramme-molecules per litre of bromine must have been used up to form different molecular aggregates. The solution of bromine in carbon bisulphide is supposed to be so concentrated that the changes in its concentration are negligible.

* Assume that the reaction in the aqueous layer is



Let the concentration of $\text{Br}_3^- = C$, of free $\text{Br}_2 = C_2$, of $\text{Br}^- = C_1$; then from the law of mass action

$$C_1 \times C_2 = K \times C.$$

But from the above it is seen that

$$C_1 = A - (B - D),$$

$$C_2 = D,$$

$$C = B - D,$$

and therefore that

$$K = \frac{D[A - (B - D)]}{B - D}.$$

The following results were obtained by Roloff¹, at 32.6° C., indicating that the complex tribromide is formed.

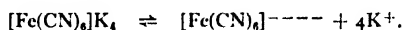
D.	B.	A.	K.
0.0264 (water)	—	—	—
0.0261	0.1111	0.250	0.0508
0.0259	0.0686	0.125	0.0500
0.0257	0.0472	0.0625	0.0488

The Ionic Migration Method.—When a current of electricity passes through an electrolyte, the cations and anions generally move with different velocities; e.g. in an aqueous solution of sodium chloride, the relative velocities of the sodium and chloride ions are as 43.5 to 65.5, i.e. the chlorine ions leave the space around the

¹ *Zeit. Phys. Chem.*, 13, 341 (1894).

cathode more rapidly than the sodium ions leave the space around the anode, and the fraction of the total current carried by the two ions can be found by measuring the change in concentrations in the liquids around the electrodes. The analysis also indicates what elements are present in the cation and anion, and their relative amounts. Thus Hittorf¹ studied the electrolysis of potassium ferrocyanide, and we will consider the numerical results which he obtained.

13.7207 gm. of the solution before electrolysis gave, when evaporated with sulphuric acid and ignited, 2.0505 gm. of potassium sulphate and 0.4869 gm. of ferric oxide; 23.3087 gm. of the solution from the anode chamber after electrolysis gave 3.2445 gm. of potassium sulphate and 0.8586 gm. of ferric oxide. During the passage of the current 0.5625 gm. of silver was deposited on the cathode of a voltameter. The above analysis shows that the anode solution after electrolysis contained 1.4585 gm. of potassium and 0.60096 gm. of iron. In potassium ferrocyanide 1.4585 gm. of potassium are equivalent to 0.5281 gm. of iron. There was thus an excess of iron in the anode chamber, and this excess is equal to 0.60096 — 0.5281 gm. 0.07286 gm. = 0.002602 equivalent. The silver deposited, 0.5625 gm., is 0.00521 equivalent. It follows, therefore, that the valency of an ion containing one equivalent of iron is 0.00521/0.002602, or the valency of the complex ion containing one atom of iron is $2 \times 0.00521/0.002602 = 4$. Similarly the deficit in potassium corresponding to two equivalents of iron is 4 grammes-atoms. Hence the formula of the complex ion must be $[\text{Fe}(\text{CN})_6]$, and the ionization of the salt in water can be represented as follows:



Electromotive Force Measurements.—The electrode potential of a metal in contact with a solution of one of its salts is a measure of the concentration of the metallic ion in solution. Thus copper in contact with a solution of potassium cuprocyanide indicates a very low concentration of copper ions compared with that given by an ordinary copper salt in equal total concentration. This indicates that in the former case either practically all the copper is present in the form of a complex ion, or that the salt is but slightly ionized in solution. Measurements of electromotive force are generally employed to determine the stability of complex ions and will be discussed fully later.

¹ *Pogg. Ann.*, 89, 117; 98, 1; 103, 1; 106, 337, 513 (1853-9).

Rhase-rule Method.—This will be treated in the chapter dealing with the stability of complex salts.

Colour.—A change in colour generally accompanies the formation of a complex salt. Cobalt salt solutions are pink, this being the colour of the cobalt ion. The complex oxalates and malonates of cobalt yield green solutions, the complex anions $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{Co}(\text{C}_3\text{H}_2\text{O}_4)_3]^{3-}$ being dark green in colour. Copper salt solutions are blue, whereas a solution of potassium cuprocyanide is colourless, indicating complex salt formation.

CHAPTER III

Types of Inorganic Complex Salts

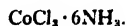
Introduction.—The methods of study discussed in the preceding chapter are applicable to all types of inorganic complex salts. For convenience of treatment we shall now study those compounds which possess central atoms with a co-ordination number equal to six. The properties of these compounds will be treated in fair detail and correlated with the formulae ascribed to them by Werner, whose method of formulation will be adopted in this book. The methods of study which have already been discussed will be applied to this end.

COMPOUNDS WITH CO-ORDINATION NUMBER SIX

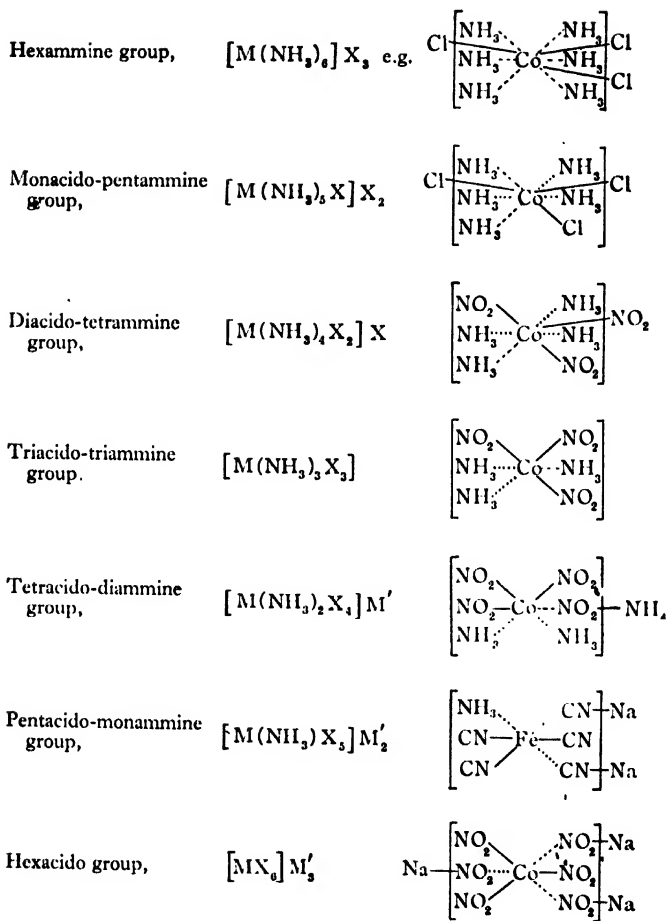
These compounds with a co-ordination number equal to six fall easily into the groups shown on the following page.

THE HEXAMMINE GROUP

Hexamine-Cobaltic Chloride.—If one leads a current of air through a solution containing cobaltous chloride, ammonium chloride, and ammonia, several cobaltamines are formed. These can be separated by fractional crystallization, and a yellow substance can be isolated having the composition



Addition of silver nitrate to a solution of this compound produces an immediate precipitate of silver chloride in the cold; quantitative



where M represents a trivalent metal, M' a univalent metallic radicle and X a univalent acidic radicle. In the structural formulæ the continuous and dotted lines represent principal and auxiliary valencies respectively.

analysis shows that the whole of the chlorine is thus precipitated and the corresponding nitrate $\text{Co}(\text{NO}_3)_3 \cdot 6\text{NH}_3$ remains in solution. By the action of warm concentrated sulphuric acid on the above chloride, hydrochloric acid gas is evolved, and the corresponding sulphate, $\text{Co}_2(\text{SO}_4)_3 \cdot 12\text{NH}_3$, remains in solution. Similarly the three chlorine atoms can be replaced by the equivalent amount of any other acidic radicle by the ordinary method of double decomposition; e.g. the addition of potassium oxalate to a concentrated solution of the chloride produces a precipitate of the oxalate. In the same way the three chlorine atoms may be replaced by more than one acidic radicle to give such compounds as $\text{CoClBr}_2 \cdot 6\text{NH}_3$, $\text{Co}(\text{NO}_3)\text{SO}_4 \cdot 6\text{NH}_3$, &c. If one adds silver oxide to a solution of the chloride a strongly alkaline solution is obtained which readily absorbs carbon dioxide from the air. The base thus formed has the composition $\text{Co}(\text{OH})_3 \cdot 6\text{NH}_3$, the three chlorine atoms having been replaced by the three hydroxyl groups. An aqueous solution of hexammine-cobaltic chloride reacts neutral, it does not taste or smell of ammonia, and the solid salt may be heated with fuming hydrochloric acid without undergoing decomposition. In the cold, alkali has no effect on the compound, but on warming ammonia is evolved and a black precipitate of cobaltic oxide is formed. The same condition of temperature applies to the precipitation of cobalt by a carbonate or a phosphate. Ammonium sulphide, however, produces an immediate precipitate of black cobaltous sulphide in the cold.

These experiments indicate that, in aqueous solution, the salt behaves in exactly the same way as any ordinary salt chloride, and consequently we infer that the three chlorine atoms are present in solution as chloride ions. The usual tests for ammonium ions give negative results, showing that the six ammonia molecules are very firmly held in the molecule. The tests applied for the presence of cobalt ions indicate that the concentration of these ions in the solution is very low (cf. chapter on Inorganic Complex Salts and Qualitative Analysis).

The molecular weight of the salt in dilute solutions as found by the freezing-point method indicates that it dissociates into four ions, i.e. the value found is practically one-quarter of the empirical formula. The molecular conductivity at a dilution of 1024 litres also indicates a quaternary electrolyte. For $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\mu_{1024} = 432$. Cf. AlCl_3 , $\mu_{1024} = 413$.

From these results we may safely conclude that an aqueous solution of hexammine-cobaltic chloride dissociates, giving a complex

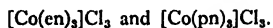
causing Co , 6NH_3 and three chloride ions. Werner suggested formulating the compound thus:



The part inside the square brackets forms a complex ion, in this case a complex cation, and the chlorine atoms outside the square brackets give chloride ions in solution. The salt therefore behaves as an ordinary salt chloride. In this compound cobalt is tervalent and has its three valencies satisfied by the three univalent chloride atoms. How then are the six ammonia molecules held in the molecule? Werner at first assumed the existence of two kinds of valencies which he called principal and auxiliary valencies. Atoms whose principal valencies were satisfied were supposed to have residual valencies which could be brought into play to satisfy the residual valencies of other atoms or groups. In the above case the residual valencies of cobalt satisfy the residual valencies of nitrogen in the six ammonia molecules. This question is treated in detail in another part of the book.

In these compounds the part inside the square brackets is known as the "co-ordinated complex". Since the central atom in this case has associated with it six ammonia molecules, the co-ordination number is said to be six. The co-ordination number six is very common in complex salts, but other values are also found, four being fairly common.

The six ammonia molecules in hexammine-cobaltic chloride may be substituted by other similar molecules containing tervalent nitrogen without changing the general character of the compound. Thus two molecules of ammonia may be replaced by one molecule of ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (in future referred to as "en"), which contains two nitrogen atoms, or by one molecule of propylenediamine ($=\text{pn}$), $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$. We thus have compounds of the type



In these two compounds the six molecules of ammonia have been replaced by three molecules of these diacid bases. This substitution may be carried out in stages and the intermediate compounds, $[\text{Co}(\text{NH}_3)_4(\text{en})]\text{Cl}_3$ and $[\text{Co}(\text{NH}_3)_2(\text{en})_2]\text{Cl}_3$, isolated. The hydroxylamine molecule may also replace ammonia, whereby the compound

¹ *Ber.*, 40, 15 (1907). This article gives a very complete list of references to inorganic complex salts to the end of 1906.

$[\text{Co}(\text{NH}_2\text{OH})_6]\text{Cl}_3$ is produced. It is thus seen that a large number of different compounds can be obtained by the partial or total replacement of ammonia molecules by the molecules of other basic nitrogen compounds.

Similar compounds are known with other metals as the central atom; all metals, however, do not possess the same tendency to complex salt formation. The readiness with which metals play the part of central atoms in complex salts appears to increase with decreasing electroaffinity of the metal. Thus, complex salts with the alkali metals as central atoms are not known, whereas many of the compounds of the noble metals are complex in nature, e.g. platinum, silver, and gold. Similarly the anions of the weaker acids enter the co-ordinated complex much more readily than the anions of the stronger acids; cf. the number of complex cyanides. The tendency to complex salt formation is treated in Chapter XI.

Replacement of the central cobalt atom by tervalent chromium, iridium, or rhodium gives hexammine compounds of the following type:



where N represents NH_3 , $\frac{1}{2}\text{en}$, $\frac{1}{3}\text{pn}$, &c., and X represents a univalent acidic radicle or its equivalent. In these cases one finds three univalent acidic radicles or their equivalent outside the co-ordinated complex corresponding to the tervalency of the central atom.

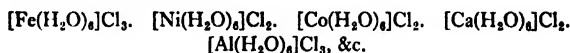
Platinum can also play the part of the central atom; this metal is, however, quadrivalent and requires four equivalents of acidic radicles to satisfy its four valencies. The formula for hexammine-platinic chloride thus becomes $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$. The triethylenediamine and tripropylenediamine compounds would have corresponding formulæ.

Several bivalent metals also can play the part of central atoms in analogous compounds, and in these cases two equivalents of acidic radicle are found outside the complex. The general formula for these compounds is $[\text{M}(\text{N})_6]\text{X}_2$. In the case of iron the ammonia compound is not known, but a similar type of compound of ferrous iron co-ordinated with three molecules of dipyridine can be prepared; the chloride of this complex would have the formula $[\text{Fe}(\text{dipy})_3]\text{Cl}_2$.¹

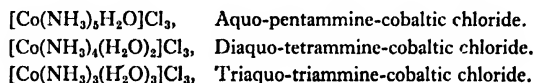
Hydrates.—A large number of inorganic salts crystallize with six molecules of water of crystallization. This suggests a relation-

¹ *Blau Monatsh.*, 19, 647 (1898).

ship to the hexammine compounds. These hydrates cannot be formulated by the ordinary valencies, and Werner gave them the co-ordination formulæ, e.g.



The water molecules are thus regarded as being in the complex, playing the same part as the ammonia molecules in the ammines. The acidic radicle is outside the complex and therefore dissociates as an ion in aqueous solution. The assumption of a close relationship between the ammines and the hydrates is supported by the fact that mixed compounds can be prepared; for example:

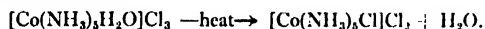


It is seen that in these compounds the total number of molecules (water-ammonia) associated with the central atom is six.

THE MONACIDO-PENTAMMINE GROUP

On bubbling air through a solution containing cobaltous chloride, ammonium chloride, and ammonia (as in the preparation of hexammine-cobaltic chloride), there is also formed a compound having the composition $\text{CoCl}_3 \cdot 5\text{NH}_3$. This compound differs from the hexammine compound in having one molecule fewer of ammonia. Qualitative analysis shows that the cobalt atom and the ammonia molecules behave in the same way as in the hexammine compound; the same applies to two of the three chlorine atoms, which can be precipitated in the cold by silver nitrate, replaced by other acidic radicles, &c. The third chlorine atom, however, is held much more firmly and will react only at higher temperatures. Thus a quantitative estimation of chloride by the usual method would give a result two-thirds of that obtainable after a thorough decomposition of the molecule has taken place. Molecular weight determinations by the cryoscopic method indicate a ternary electrolyte. This is further confirmed by the value of the molecular conductivity $\mu_{1024} = 261$ (cf. for MgCl_2 , $\mu_{1024} = 235$). These results can be explained only by assuming that in aqueous solution two of the three chlorine atoms dissociate as ions, and that a complex cation containing cobalt, five ammonia molecules, and one chlorine atom is formed. The

compound is thus given the formula $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$; its aqueous solution contains the ions $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+1}$ and 2Cl^- . This compound, which is known as chloro-pentammine-cobaltic chloride, can also be prepared by heating aquo-pentammine-cobaltic chloride, a compound already mentioned in the hexammine group (p. 26). This aquo complex contains a molecule of water in the first sphere; and on heating it the molecule of water contained in the complex is driven off and its place taken by a chlorine atom. The change can be represented thus:

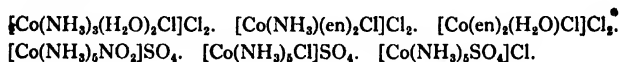


The one chlorine atom which has now entered the co-ordinated complex is held so firmly that it is not dissociated in aqueous solution. From this behaviour Werner concluded that, before a salt can dissociate in solution, foreign molecules must enter between the metallic and acidic radicles. In hexammine-cobaltic chloride, the central cobalt atom is surrounded by six ammonia molecules which fill up the first sphere; the three chlorine atoms, being in the second sphere and some distance away from the cobalt atom, are easily dissociated. In the aquo-pentammine compound the six places in the first sphere are occupied by five ammonia molecules and one water molecule, and the three chlorine atoms are again easily dissociated. If now this water molecule is expelled from the latter compound, a chlorine atom goes from the second to the first sphere to take its place, and is thus in close proximity to the central atom and therefore non-ionizable. A difficulty arises when one considers the ionization of a simple salt. How, according to this theory, does one account for the ionization of, say, ferric chloride in aqueous solution? Werner assumes that when a simple salt is dissolved in water it is immediately converted into a complex aquo salt, water molecules entering the first sphere and thus separating the metallic from the acidic radicles. According to this theory, a solution of ferric chloride contains the complex salt hexaquo-ferric chloride, $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$. This formation of aquo complexes is not, however, supported by molecular weight determination of the solute.

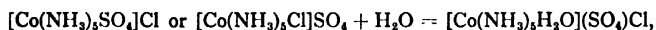
The three principal valencies of cobalt in the pentammine compound are satisfied by three chlorine atoms as in the hexammine derivative. In the former case, however, one of the three chlorine atoms is in the first sphere, which leaves two outside the complex to form ions; the valency of the complex is thus seen to be two. In general the valency of the complex is equal to the valency of the

central atom minus the number of univalent negative groups, or their equivalent, in the first sphere. This will be easily understood as we pass from one type to the other.

The ammonia molecules can again be replaced by other nitrogen compounds or water, &c., as was found to be the case with the hexammine group. The chlorine atoms can also be replaced by other acidic radicles, and the following compounds, among others, can be obtained:

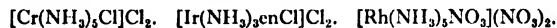


It is interesting to note that in the last compound the bivalent sulphate radicle occupies only one co-ordination position in the complex, though it satisfies two valencies of the central cobalt atom; the co-ordination complex is thus univalent. The compound preceding it is its isomer, and it is seen that in this the complex is bivalent, the chlorine atom being in the first and the sulphate radicle in the second sphere. These two compounds are unstable, and readily undergo change in aqueous solution to give a compound of the hexammine type, thus:



the product being aquo-pentammine-cobaltic sulphate chloride.

Similar pentammine compounds are formed by other metals as discussed under the hexammine type, e.g.



Brief mention may be made here of the hexahydrates of chromium chloride¹ which are known to exist in three forms: (1) the violet β salt, (2) the green γ salt, (3) the green α salt. These three salts have each the composition corresponding to the formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. The co-ordination theory gives an explanation of the isomerism and assigns a definite structure to each salt.

The violet salt can be formed by passing hydrogen chloride into a saturated solution of chromic oxide in hydrochloric acid at a low temperature, 8° to 10° C. A solution of this salt reacts with silver nitrate in the cold, producing a precipitate of silver chloride, all the chlorine being thus precipitated. The molecular conductivity indicates a quaternary electrolyte, $\mu_{1024} = 435$ (cf. AlCl_3 , $\mu_{1024} = 416$). The salt does not lose any of its water of crystallization when kept in

¹ Werner, *Ber.*, 34, 1579 (1901).

a vacuum desiccator over sulphuric acid; this indicates that the water molecules are very firmly held in the molecule. These properties suggest that the violet salt is hexaquo-chromic chloride having the formula $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$. This is thus a salt corresponding to the hexammine type.

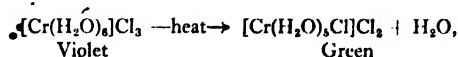
The green γ salt can be prepared by heating the violet salt to 70°C . and saturating it with hydrogen chloride. A solution of this salt reacts with silver nitrate, but, if the reaction is carried out in the cold, the precipitated silver chloride corresponds to two only of the three chlorine atoms. Molecular conductivity measurements, which must be carried out at 0°C ., yield the value for ternary electrolytes, $\mu_{1024} = 125$ (μ_{1024} for ternary electrolytes at 0°C . = 131). The green γ salt loses one molecule of water if placed in a vacuum desiccator over sulphuric acid, without, however, changing its general character. One therefore concludes that the loosely held molecule of water is outside the complex, whereas the firmly held molecules form a part of the complex. The green γ salt is therefore given the formula $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ - monohydrated chloro-pentaquo-chromic chloride.

The green α salt (obtained by crystallization of a chromic chloride solution at 0°C .), on the other hand, behaves as if it had the formula $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$, i.e. it is a salt belonging to the tetrammine type, which will be considered in the next section.

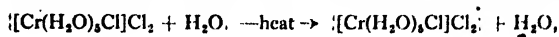
We thus see the method employed for determining whether or not the molecules of water of a hydrate are in the co-ordinated complex.

1. If the water molecules are in the first sphere they are held very firmly and are not lost when the salt is placed in a vacuum desiccator over sulphuric acid.

2. The removal of a molecule of water from the complex changes the character of the compound:

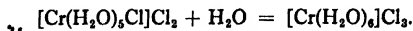


i.e. the salt changes from the hexammine to the pentammine type. If on the other hand the molecule of water lost does not come from the complex, then the character of the compound remains unchanged:



i.e. the salt still belongs to the pentammine type.

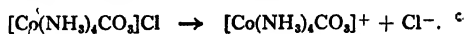
It was mentioned above in the case of the green γ salt that the molecular conductivity must be determined at 0°C .; the conductivity rapidly increases with the temperature. This rapid increase is due to hydration, as shown by the following equation:



A molecule of water displaces the atom of chlorine in the complex and the salt changes in character—being now a salt of the hexamine type. The molecular conductivity increases from a value corresponding to that of a ternary electrolyte to that of a quaternary electrolyte. This hydration also affects the precipitation with silver nitrate; the precipitation must be carried out in the cold, otherwise the reaction of the hydrated compound is obtained. In elucidating the structure of an inorganic complex salt, all reactions should be carried out in the cold, as many of these complexes are unstable at higher temperatures.

THE DIACIDO-TETRAMMINE GROUP

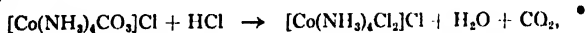
If one leads a rapid current of air through a solution containing cobaltous chloride, ammonia, and a large excess of ammonium carbonate, one can obtain from the solution a compound having the composition $CoCO_3 \cdot Cl \cdot 4NH_3$. The chlorine in this compound is immediately precipitated in the cold by silver nitrate, indicating its presence as an ion in solution. Barium or calcium chloride produces no precipitate of the carbonate, thus showing the absence of carbonate ions. The ammonia molecules behave as in the case of the hexamine and pentamine complexes, being firmly held in the molecule. Alkali gives no precipitate in the cold, but on warming a black precipitate of cobaltic oxide is produced; cobalt is therefore trivalent in this compound. Molecular weight and molecular conductivity determinations indicate a binary electrolyte, $\mu_{1024} = 96$ (μ_{1024} for $NaCl = 118$). We must therefore conclude that in aqueous solution the compound dissociates, giving a chloride anion and a complex cation containing the central metallic atom cobalt, four ammonia molecules, and the carbonate radicle:



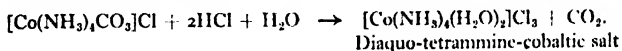
The cation is here univalent, two of the three valencies of the central cobalt atom being satisfied by the bivalent carbonate radicle which

is inside the complex. The compound is known as carbonato-tetrammine-cobaltic chloride. It is here seen that the bivalent carbonate radicle occupies two positions in the co-ordinated complex, whereas the bivalent sulphate radicle in sulphato-pentammine cobaltic chloride, $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$, only occupies one position in the first sphere.

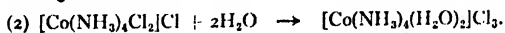
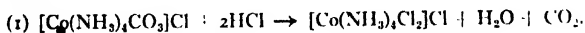
The carbonate radicle in this compound can be replaced by another acidic radicle by the action of the acid in question, thus (concentrated HCl in the cold):



the corresponding dichloro-tetrammine compound being formed. If, however, the hydrochloric acid employed is very dilute and the reaction allowed to take place at higher temperatures, the product is different and a compound of the hexammine type is produced:



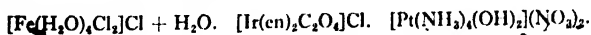
This reaction can be regarded as taking place in two stages: (1) the replacement of the carbonate group by two chlorine atoms as in the first case; (2) the hydration of the dichloro compound produced by (1):



Similarly nitrous acid reacts with the carbonato compound to give the corresponding dinitro derivative, $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{Cl}$.

Again the ammonia molecules can be replaced by other nitrogen compounds or by water to give a large number of compounds. Thus the green α chromic chloride discussed in the last section belongs to the tetrammine type, the four ammonia molecules being replaced by four molecules of water, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} + 2\text{H}_2\text{O}$.

The central cobalt atom may further be replaced by other metals to give analogous compounds.



The platinum complex above is bivalent, the platinum being quadrivalent; it is also interesting to note that in this compound the two negative groups inside the complex are hydroxyl groups.

THE TRIACIDO-TRIAMMINE GROUP

A compound having the composition $\text{Co}(\text{NO}_2)_3\text{NH}_3$ is obtained by bubbling air through a solution containing cobaltous chloride, sodium nitrite, and ammonia in the molecular proportions 1 : 4.6 : 26. It is brown in colour and is but slightly soluble in cold water. In the cold, analytical reactions do not indicate the presence of cobalt ions, nitrite ions, or ammonia. Its aqueous solution is a non-conductor of electricity, and cryoscopic determinations of the molecular weight give the theoretical value. These results indicate that the salt does not ionize in solution, and it is therefore formulated $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$. The three principal valencies of cobalt are here satisfied by three negative groups which are themselves in the coordinated complex, and therefore no group is found outside the first sphere. By the action of fairly concentrated hydrochloric acid on this trinitro-triammine cobalt, one nitro group is replaced by a chlorine atom to give chloro-dinitro-triammine cobalt, $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_2\text{Cl}]$; this structure indicates that an aqueous solution of the complex is a non-conductor of electricity. It is, however, found that it has an appreciable conductivity, and that this conductivity increases rapidly on allowing the solution to stand, as is shown by the following table:

		Temperature, 0°C. ν -- 256.					
Time (in seconds)	..	0	2	5	17	30	
μ	29	32	35	39	41

This increase in the conductivity is due to hydration, which takes place gradually in solution.



This hydration produces a binary electrolyte, the product being dinitro-aquo-triammine-cobaltic chloride, a complex of the tetrammine type. A freshly prepared solution gives no precipitate with silver nitrate, but on standing a precipitate of silver chloride is gradually formed; this is the natural result of the above reaction. The rate of hydration can be measured by the rate of increase in the electrical conductivity.

The same variety of compounds is met with in this group as in the others; the ammonia molecules can be replaced by other similar molecules and the central cobalt atom by other metallic atoms.

The triacido-triammines of trivalent metals (cobalt, chromium, iron, &c.) are non-electrolytes, because the three valencies of the

THE TETRACIDO-DIAMMINE GROUP

central atom are satisfied by three univalent negative groups, or their equivalent, in the complex. In the case of quadrivalent platinum, on the other hand, the fourth valency of the central atom is satisfied by a group outside the complex and the compound is a binary electrolyte; cf. trichloro-triammine-platinic chloride, $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$. The non-electrolyte in the case of quadrivalent platinum is a complex of the diammine type, which will be discussed in the next section.

An amino acid can enter the co-ordinated complex, the principal valencies of the central atom being satisfied by the principal valency of the carboxyl group, and the amino group being attached to the central atom by means of auxiliary valencies. Thus in the case of cobalt as the central atom and glycocoll as the amino acid we have the complex salt $\left[\text{Co} \left(\begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{O} - \text{CO} \quad \text{CH}_2 \end{array} \right) \right]$, belonging to the triacido-triammine type of compound. These complex salts, which have a principal and auxiliary valency of the central atom attached to different parts of the same molecule, are known as inner complex salts.

THE TETRACIDO-DIAMMINE GROUP

A solution containing cobaltous chloride, sodium nitrite, ammonium chloride, and ammonia in the molecular proportion 1 : 5·2 : 5·0 : 0·72, on being oxidized by a current of air, will deposit crystals having the composition $(\text{NH}_4)\text{Co}(\text{NO}_2)_4\cdot 2\text{NH}_3$. The results of investigations, as discussed for the other types, indicate that the compound is a binary electrolyte giving ammonium as the cation and a complex anion containing the cobalt atom, two ammonia molecules, and four nitro groups. Hence it is formulated $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{NH}_4$, being a salt of the acid $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]\text{H}$. In this complex salt the three valencies of cobalt are satisfied by three of the four nitro groups in the complex; the fourth nitro group, has still a principal valency to be satisfied, necessitating a positive group or atom outside the complex. The net result is that the complex has a negative valency of one. This salt is known as Erdmann's salt,¹ after its discoverer; according to the complex salt nomenclature it is called ammonium tetranitro-diammine cobaltate, being the ammonium salt of tetranitro-diammine-cobaltic acid. By the action of oxalic acid on the tetranitro compound, two of the four nitro

¹ *Journ. f. prak. Chem.*, 97, 406 (1866).

groups are replaced by the bivalent oxalate radicle, giving ammonium oxalato-dinitro-diammine cobaltiate, $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]\text{NH}_4$.

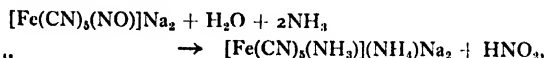
It is readily seen that a large number of compounds are possible by replacement of the groups inside the complex by other similar groups.

As already mentioned in the last section, the diammine compound of quadrivalent platinum is a non-electrolyte; e.g. tetrachloro-diammine platinum, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$.

THE PENTACIDO-MONAMMINE GROUP

As the general name indicates, the compounds of this type contain only one molecule of ammonia. Such compounds with cobalt or chromium as central atoms are not known, but in the case of iron a compound of the following composition can be prepared, $\text{FeNH}_3(\text{CN})_5\text{Na}_2\text{H}_2\text{O}$. Qualitative tests indicate the presence of sodium ions in solution and a complex anion. The molecule of water is readily eliminated in a vacuum desiccator, the character of the compound being unchanged; this shows that the water does not form a part of the co-ordinated complex. Physical measurements point to the fact that the salt is a ternary electrolyte; it thus receives the formula $[\text{Fe}(\text{NH}_3)(\text{CN})_5]\text{Na}_2 + \text{H}_2\text{O}$, being sodium pentacyano-monammine ferriate. Sodium nitroprusside is another example of a salt of this type, $[\text{Fe}(\text{NO})(\text{CN})_5]\text{Na}_2$; it contains a nitroso group instead of the molecule of ammonia, and can be called sodium pentacyano-nitroso ferriate.

If one treats sodium nitroprusside with ammonia, the nitroso group is replaced by an ammonia molecule, and at the same time there occurs a reduction of ferric to ferrous iron to form a pentacido monammine of ferrous iron,¹ thus:



the nitroso group being oxidized to nitrous acid. The product of this oxidation (disodium-ammonium-pentacyano monammine ferriate) gives reactions in conformity with the given formulation. The complex in this case is tervalent, because the valency of ferrous iron can only satisfy two of the five cyano groups; the valencies of the three remaining cyano groups have therefore to be satisfied by three positive groups outside the complex.

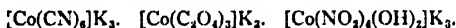
¹ Hofmann, *Ann. Chem.*, **312**, 1 (1900).

In the case of chromium, compounds belonging to this type are known containing a water molecule in place of the ammonia. Thus a potassium salt having the composition and properties in agreement with the formula $[\text{Cr}(\text{H}_2\text{O})\text{Cl}_5]\text{K}_2$ is well known, as are also the analogous rubidium and caesium salts. In the case of lithium, the compound contains five molecules of water, one only being in the first sphere; thus $[\text{Cr}(\text{H}_2\text{O})\text{Cl}_5]\text{Li}_2 \cdot 4\text{H}_2\text{O}$. These four molecules of water are readily expelled, but the fifth, which forms a part of the co-ordination complex, is not removed at 160°C .

THE HEXACIDO GROUP

This group is represented by several well-known compounds. Potassium cobalti-nitrite has the composition $\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$, and it was generally represented by that formula, indicating a double salt. This does not, however, interpret the reactions of the compound. The six nitro groups are firmly held in the molecule, the compound being stable in acetic acid solution. There is no reaction with dilute hydrochloric or nitric acids in the cold; on warming, however, the nitro groups are expelled. Cryoscopic determinations of the molecular weight in dilute solutions indicate a quaternary electrolyte, a conclusion which is confirmed by measurements of molecular conductivity. Analytical reactions show that the ions present are potassium cations and a complex anion containing cobalt and the six nitro groups. The compound is thus formulated $[\text{Co}(\text{NO}_2)_6]\text{K}_3$, and according to the complex salt nomenclature is called potassium hexanitro cobaltate.

Many other similar compounds of cobalt can be prepared containing other acidic radicles, e.g.



It is seen that each oxalate radicle occupies two positions in the co-ordinated complex. In the third example given two hydroxyl groups have replaced the equivalent acid.

Similar compounds of chromium and iron are also well known. In the case of the latter, compounds of ferrous and ferric iron are common, e.g. potassium ferrocyanide, $[\text{Fe}(\text{CN})_6]\text{K}_4$ (potassium hexacyano ferrite), and potassium ferricyanide, $[\text{Fe}(\text{CN})_6]\text{K}_3$ (potassium hexacyano ferrate), the former giving a quadrivalent and the latter a trivalent complex anion.

Cryolite is another example of a complex hexacido salt, in which the central atom is aluminium: $[\text{AlF}_6]\text{Na}_3$. This is a very unstable complex salt which breaks up in solution into sodium fluoride and aluminium fluoride. For this reason it is generally formulated as a double salt of these components, $\text{AlF}_3 \cdot 3\text{NaF}$. The stability of complex salts will be treated in a later chapter.

If the central atom is quadrivalent, then the complex anion becomes bivalent, as in the case of potassium platinichloride, $[\text{PtCl}_6]\text{K}_2$, and potassium fluosilicate, $[\text{SiF}_6]\text{K}_2$.

CHAPTER IV

Spatial Arrangement and Isomerism

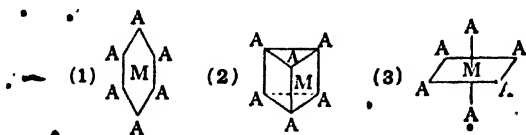
In the compounds so far considered, we have a co-ordinated complex containing six univalent groups, or their equivalent, around the central atom. The question naturally arises: how are these groups arranged in space? The tetrahedral arrangement of groups around the carbon atoms in organic compounds has been adopted because it explains the isomerism of these compounds. In the same way the spatial arrangement of groups in the first sphere around the central atom must explain the isomerism of the inorganic complex salts.

Compounds with six similar groups around the central atom, e.g. $[MA_6]$, exist only in one form. If one of the six groups is replaced by another group, the product is always the same, i.e. no isomers of compounds of the type $[M(A)_5B]$ are known. B might have replaced any one of the six A groups, and since one and only one product is obtained, it follows that the six groups are symmetrically arranged around the central atom. This is possible in three ways:

(1) The groups can be arranged at the six corners of a regular hexagon in the same plane as the central atom (cf. benzene).

(2) The groups can be placed at the corners of a triangular prism with the metal at the centre.

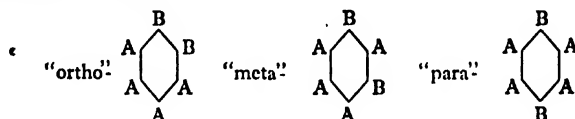
(3) The groups can be arranged at the six corners of a regular octahedron with the metal at the centre.



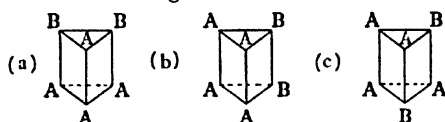
These three configurations satisfy the above requirements, since these are all symmetrical with regard to the central atom. Replacement of any one of the A groups leads to the same product.

If another A group is replaced by another B group to form a compound of the type $[MA_4B_2]$, it is found that two isomers and only two are produced. This result can now be applied to the above configurations.

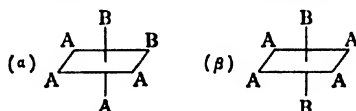
(1) The hexagonal arrangement would give three isomeric products, corresponding to the ortho, meta, and para diderivatives of benzene, as follows:



(2) The triangular prism configuration would also allow the production of three isomers. In (a) the two B groups are in the same triangular plane, in (b) they are in different triangular planes but are on a common edge, whereas in (c) they are neither in the same plane nor on a common edge.



(3) The octahedral arrangement, on the other hand, allows of the formation of only two isomers as represented by α and β . In (a) the two B groups are on adjacent corners of the octahedron, whereas in (β) they are on opposite corners. The apices are of equal value, being symmetrically arranged around the central atom, hence it is only their relative positions that are of importance.

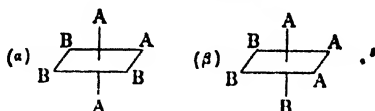


It is thus seen that the number of isomers of the compounds formed by the replacement of two A groups by two B groups is satisfied by the octahedral arrangement, as is also the non-existence of mono-substituted derivatives.

We will now consider the case where three A groups are replaced by three B groups. Two isomeric derivatives are obtained by experiment, and on applying the above octahedral arrangement, it is found

DETERMINATION OF THE CONFIGURATION 49

that this admits of only two products. The configurations of these isomers are shown below; in (a) the three similar groups are in the same plane, in (β) they are in different planes.



The reader should satisfy himself by working with octahedral models that only two isomeric products are possible.

When four A groups are replaced by four B groups, a compound of the type $[MA_2B_4]$ is obtained, which is analogous to the disubstituted derivative as far as isomerism is concerned, cf. $[MA_4B_2]$. It will be seen in the next chapter that very strong evidence in favour of this spatial arrangement brought forward by Werner is afforded by the existence of optically active salts with a complex of the type $[MX_3]$, where X is a radicle occupying two positions in the co-ordinated complex.

DETERMINATION OF THE CONFIGURATION

It has already been noted that compounds of the type $[MA_2B_4]$ can exist in two isomeric forms. This was first discovered by Jørgensen¹ in 1890 in the case of $[Co(en)_2Cl_2]Cl$. These isomers have different properties—solubility, colour, reactivity, &c. Jørgensen's nomenclature of these complex salts was based on their colour. In the above case the one isomer was found to be green and was therefore called praseo-dichloro-diethylenediamine-cobaltic chloride, the other isomer being violet and known as the violeo-salt. The two isomeric compounds² having the formula $[Co(NH_3)_4Cl_2]Cl$, being yellow and green, were known as the croceo- and praseo-dichloro-tetrammine-cobaltic chloride respectively. Similarly, the brown and yellow isomers³ of $[Co(en)_2(NO_2)_2]X$ were called the flavo- and croceo-dinitro-diethylenediamine salts respectively. These names simply indicated the colour of the isomeric salts, and gave no information as to their structure.

Werner,⁴ having formulated the octahedral theory, endeavoured to find the exact structure of the isomers. His experiments led him

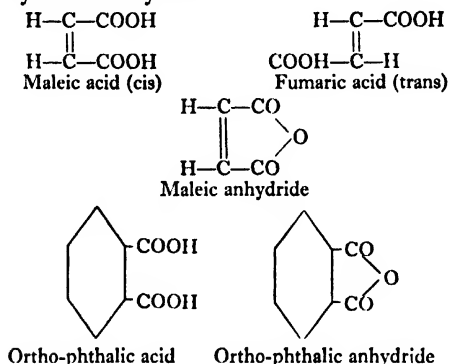
¹ *Journ. f. prakt. Chem.*, 41, 440 (1890).

² Werner and Klein, *Zeit. anorg. Chem.*, 14, 28 (1897).

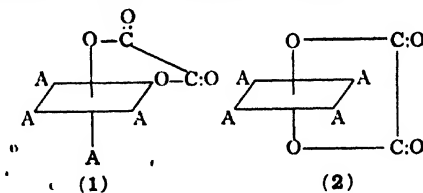
³ Werner and Humphrey, *Ber.*, 34, 1720 (1901). ⁴ *Ann.*, 386, 1 (1912)

COMPLEX SALTS

to the conclusion that this isomerism was of the *cis-trans* type so familiar in organic chemistry. Thus in the case of the two isomers *maleic* and *fumaric* acids, the former is supposed to have the *cis* structure because it alone gives an anhydride, indicating that the two carboxylic groups are adjacent as in the case of *ortho-phthalic* acid, which again out of the three isomeric benzene dicarboxylic acids alone yields an anhydride.

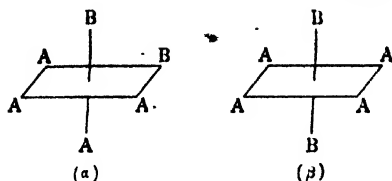


Werner's experimental application of the above principle consisted in replacing the two B groups in the compound $[\text{MA}_4\text{B}_2]$ by a group occupying two co-ordination points in the complex. If his replacement took place readily in the cold he concluded that the two B groups were adjacent and occupied the same position as the introduced groups. Since only one isomer allows of this replacement, the product was assumed to have the structure (1) in preference to the improbable (sterically) structure (2) in the following, in which two A groups are replaced by the oxalate radicle.



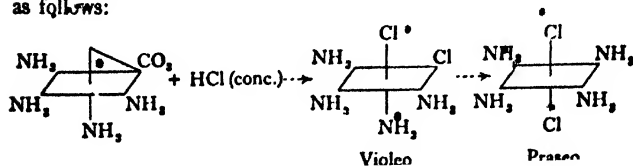
It is evident that structures (1) and (2) are derived from the original α) and β) structures respectively; and these by analogy to organic compounds are termed *cis-* and *trans-isomers*.

• DETERMINATION OF THE CONFIGURATION¹²

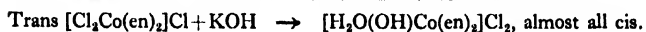
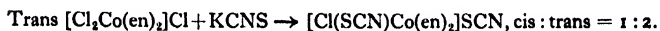


Conversely, evidence in favour of the above conclusions will be given in the next chapter when optical activity of the complex salts is discussed.

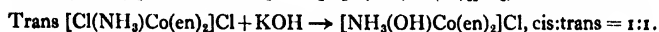
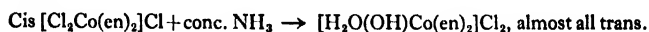
Similarly, the replacement of one group occupying two co-ordinated positions in the complex by two groups each of which occupies one position, would probably lead to the formation of the *cis* product. Thus, starting with carbonato-tetrammine-cobaltic chloride, one can replace the carbonato group by two nitro groups, this being carried out by the action of warm acidified sodium nitrite. The product formed in this case is found to be the brown dinitro-tetrammine complex; hence this is assumed to be the *cis* compound, while its yellow isomer is the *trans* compound. Again, by the action of dilute mineral acids on the carbonato complex, the carbonato group is replaced by two molecules of water and the product is taken to be the *cis*-diaquo-tetrammine complex. These configurations can be confirmed by other methods (see chapter on optical activity). By the action of concentrated hydrochloric acid on carbonato-tetrammine-cobaltic chloride, a green dichloro derivative is obtained; one concludes from this that the praseo-dichloro compound has the *cis* configuration. The other isomer, the violeo compound, changes into the green product when treated with concentrated hydrochloric acid; molecular transformation is thus possible with these compounds. If the concentrated acid is allowed to react on the carbonato complex at a low temperature, then the first product is the violeo-dichloro complex, which, however, changes rapidly into the green isomer. The violeo compound is therefore the *cis*-, and the praseo compound the *trans*-isomer, the changes which take place being represented as follows:



It is thus seen that the one isomer may be very unstable and readily undergo molecular transformation with the formation of its more stable isomer. Werner was able to show that the violet compound was first formed by carrying out the reaction at low temperatures, thus reducing the rate of transformation. The extent of these molecular transformations can be seen from the following results obtained by Werner. He started with trans-dichloro-diethylenediamine-cobaltic chloride, acted on this with different reagents, and so found that the products were often mixtures of the cis- and trans-isomers. Thus:

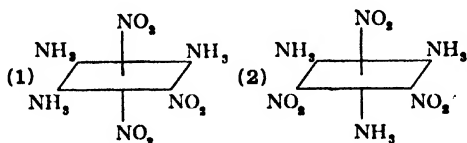


Again:



Many other results can be found in Werner's original paper.¹ No satisfactory explanation has been given of these molecular transformations (cf. Walden's inversion).

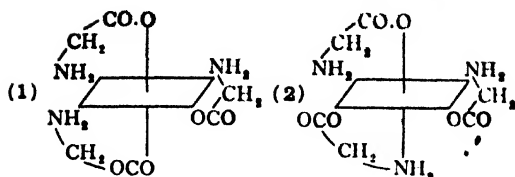
Similarly, if we consider compounds of the triacido-triammine group, e.g. $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$, the octahedral arrangement allows of the existence of two isomers, e.g.



In (1) the three similar groups (NH_3 or NO_2) are in the same plane, whereas in (2) they are in different planes. The two isomers have been isolated in a large number of cases. Ley and Winkler² have isolated two isomeric inner complex salts of cobalt and amino-acetic acid; these isomers are given the following configurations:

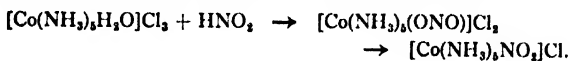
¹ *Ann.*, 386, 1 (1912).

² *Ber.*, 50, 1123 (1917).



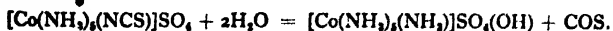
OTHER TYPES OF ISOMERISM

Structure Isomerism.—Jørgensen noticed that by the action of nitrous acid on aquo-pentammine-cobaltic chloride an unstable carmine red compound was formed which changed into a brown stable compound. Werner, later, succeeded in isolating this intermediate compound, and was able to show that it was the nitrito compound. The above reaction can thus be represented as follows:



Werner¹ was also able to prepare other nitrito compounds, and he studied their properties. He found that they were generally brick red in colour. The nitrito groups were very loosely held, being driven off by the action of dilute mineral acids. Further, they gradually changed at ordinary temperatures into the isomeric nitro compounds, this change being very rapid at 60° to 70° C. On the other hand, the nitro compounds, which are brown in colour, are very stable, not being acted upon by mineral acids (cf. nitro-methane, CH_3NO_2 , and methyl-nitrite, CH_3ONO).

The thiocyanato group can also be linked to the central atom in two ways—(1) through the nitrogen atom, (2) through the sulphur atom—to produce the isothiocyanato and the thiocyanato derivatives respectively. Thus the following two compounds are known, $[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5(\text{SCN})]\text{SO}_4$. The one isomer is readily hydrolysed into the hexammine compound, hence in this compound the thiocyanato group is linked to the cobalt atom through the nitrogen atom, the hydrolysis being represented by the following equation:

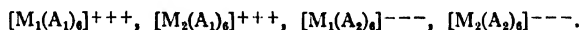


This is known as the isothiocyanato compound. The other isomer

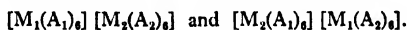
¹ Ber., 40, 768 (1907).

is not hydrolysed by acids and is not oxidized by chlorine, the cyanato group linking with the cobalt atom through the S atom, $[\text{Co}(\text{NH}_3)_5\text{SCN}]\text{SO}_4$.

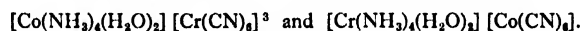
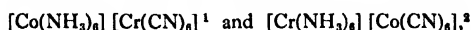
Co-ordination Isomerism.—We have already seen that a large number of molecules and groups can form a part of the co-ordinated complex. If we take two different tervalent metals M_1 and M_2 , and represent positive and negative groups by A_1 and A_2 respectively, then the following complex ions are capable of existence:



The positive cations can now combine with the anions to form salts, and the following isomeric salts will be produced:

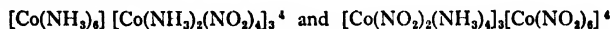


The following may be given as examples of such isomerism:

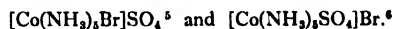


The isomerism is here due to the different distribution of the components which are co-ordinated with the central atom, and Werner called it co-ordination isomerism.

The following isomerism also belongs to this group, but is a little more complex:



Ionization Isomerism.—It has already been seen that acidic radicles do not dissociate as anions in aqueous solution if they form a part of the co-ordinated complex. This is shown by their refusal to give the ordinary analytical reactions. If a complex salt contains two acidic radicles, one of which is in the co-ordination complex and the other outside, then the existence of ionization isomers is possible, as follows:



The first compound gives a complex cation containing cobalt, five molecules of ammonia and a bromine atom, and a sulphate anion; the second compound gives a complex cation containing the

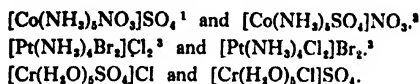
¹ Braun, *Ann.*, 125, 183 (1863).

² Jørgensen, *Journ. f. prakt. Chem.*, 30, 31 (1884).

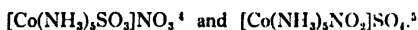
³ Pfeiffer, *Ann.*, 346, 42 (1906). ⁴ Jørgensen, *Zeit. anorg. Chem.*, 5, 182 (1894).

⁵ Jørgensen, *Journ. f. prakt. Chem.*, 19, 49 (1879). ⁶ *Ibid.*, 31, 262 (1885).

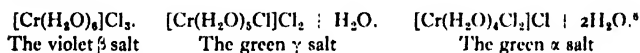
sulphate radicle and a bromine anion. The following may be given as further examples illustrating this type of isomerism:



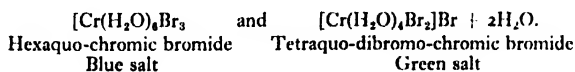
The following peculiar type of isomerism may be mentioned here:



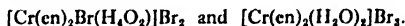
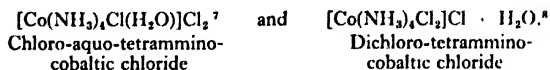
Hydration Isomerism.—This isomerism is due to the different mode of attachment of water to the complex. The best illustration is that of the hydrates of chromic chloride, which have already been discussed in Chapter III. The formulæ may be repeated:



The same relationship exists between the two isomeric chromic bromides:



Hydration isomerism is also known among the ammonia compounds:



In the last example is seen a polymerized water molecule, H_4O_2 , occupying only one position in the co-ordinated complex.

The structure of these isomers can be found by determining the readiness with which they lose water, as already discussed. Water

¹ Jørgensen, *Journ. f. prakt. Chem.*, 23, 227 (1881). ⁵ *Ibid.*, 31, 262 (1885).

² Cleve, *K. Sv. Vet. Akad. Handl.*, 10 (1872).

³ Werner, *Zeit. anorg. Chem.*, 16, 410 (1898).

⁴ Jørgensen, *Zeit. anorg. Chem.*, 5, 172 (1893).

⁵ Werner, *Ber.*, 34, 1579 (1901).

⁶ Jørgensen, *Zeit. anorg. Chem.*, 17, 465 (1898).

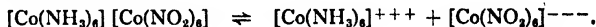
⁷ Werner, *Ber.*, 34, 1587 (1901).

forming a part of the complex is much more firmly held than when it is outside the first sphere.

Polymerism.—It is well known that benzene and acetylene have the same composition, corresponding to 92.31 per cent C and 7.69 per cent H. They have the formulæ C_6H_6 and C_2H_2 respectively. Similar phenomena are observed among the complex salts. Thus there are nine compounds which have a composition corresponding to $Co(NH_3)_3(NO_2)_3$. These compounds are formulated as follows:

1. $[Co(NH_3)_3(NO_2)_3]$.¹
2. $[Co(NH_3)_3(NO_2)_3]_2$.
3. $[Co(NH_3)_6][Co(NO_2)_6]$.²
4. $[Co(NH_3)_3(NO_2)_3]_3$.
5. $[Co(NH_3)_6NO_2][Co(NH_3)_4(NO_2)_4]$.³
6. $[Co(NH_3)_3(NO_2)_3]_4$.
7. $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]$.³
8. $[Co(NH_3)_3(NO_2)_3]_5$.
9. $[Co(NH_3)_6NO_2]_3[Co(NO_2)_4]_2$.³

It is seen that (2) and (3), (4) and (5), (6) and (7), and (8) and (9) are isomers. Compound (3) is formed by the combination of acid and basic complexes. $[Co(NH_3)_6](OH)_3$ is, for example, a tri-acidic base, and $[Co(NO_2)_6]H_3$ is a tri-basic acid. These two complexes combine together to form a salt which would ionize in aqueous solution as follows:



Compounds (5), (7), and (9) are formed in the same way. The above formulæ are proved by molecular weight determinations.

We thus see that among the complex salts various types of isomerism are found which in many cases are parallel to the isomerism found in the compounds of carbon. The correspondence between the two types of compounds as to cis- and trans-isomerism, structural isomerism, and polymerism has already been pointed out. As a parallel in the carbon series to the isomerism known in the field of complex salts as ionization isomerism, we might mention the two compounds para-bromaniline hydrochloride and para-chloraniline hydrobromide, $BrC_6H_4NH_2HCl$ and $ClC_6H_4NH_2HBr$.

Another type of isomerism which occurs in both series is accompanied by optical activity, and is traced in both cases to the existence of molecular asymmetry.⁴

¹ Erdmann, *Journ. f. prakt. Chem.*, 87, 406 (1866).

² Jörgensen, *Zeit. anorg. Chem.*, 5, 177 (1894).

CHAPTER V

Molecular Asymmetry and Optical Activity

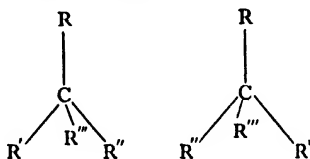
Pasteur,¹ in 1848, made the important discovery that when sodium ammonium racemate was crystallized from aqueous solution at ordinary temperatures, the crystals which separated showed hemihedral facets. Pasteur noticed that these facets were not always similarly situated, but that certain crystals were dextro-hemihedral, while others were lævo-hemihedral, so that the one crystal formed the reflected image of the other. These crystals were separated and dissolved in water. Pasteur found that the one solution rotated the plane of polarized light in one direction, and the other produced an equal rotation in the opposite direction. The free acid was then liberated from each of the active salts. The product was found to consist in the one case of dextro- and in the other of lævo-tartaric acid, and not of the racemic acid. Pasteur had thus resolved the racemic compound into its optically active components. He found that these active components were identical in all their chemical and physical properties except optical activity and crystal form. He then worked out other methods of resolution, which will be discussed later. He examined a large number of active compounds and felt convinced that hemihedral crystals indicated asymmetric molecules. Pasteur asked: Are the atoms of the dextro acid arranged in the form of a right-handed spiral or are they situated at the corners of an irregular tetrahedron? He could give no definite answer to his question, but felt convinced that the molecules of the dextro and lævo acids were non-superposable. He summarized his conclusions as follows:

1. If the atoms of an organic compound are asymmetrically arranged, this asymmetry is manifested by enantiomorphous crystalline forms.

¹ *Compt. rend.*, 26, 535; 27, 101 (1848); *Ann. de Chim. et Phys.*, 24, 442 (1846).

2. This molecular asymmetry implies optical activity.
3. The optical isomers are identical in their chemical properties (*i.e.* the asymmetric structure does not effect the chemical affinity and physical properties with the exception of those mentioned above).

The necessary conditions for optical activity were made more definite in 1874, when van't Hoff¹ and Le Bel² introduced the conception of the asymmetric carbon atom. They assumed that the four groups attached to the carbon atom were placed, or had their mean position of oscillation, at the four corners of a regular tetrahedron, with the carbon atom at the centre. This theory proved of great value, as it explained the existence of many isomers in organic chemistry. On examining a tetrahedral model for compounds of the type CR_4 , CR_3R' , $CR_2R'R''$, $CRR'R''R'''$, it will be found that only the last compound can exist in two forms and that these forms are non-superposable mirror images.



Thus when a carbon atom is joined to four different atoms or groups a molecule is formed which is non-superposable with its mirror image. Such a carbon atom was said to be asymmetric. Van't Hoff and Le Bel made the general statement that a compound must contain an asymmetric carbon atom if it is capable of existence in optically active forms, and they were able to show the presence of such an asymmetric carbon atom in all compounds which were then known to exhibit optical activity.

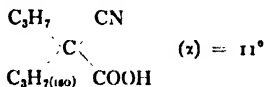
Research work in this direction was very much stimulated by the announcement of this theory, and the number of optically active compounds increased rapidly. The results of these researches confirmed the views of the Dutch and French chemists. According to this theory the existence of two enantiomorphously related isomerides should be possible whenever a plurivalent (valency > 3) asymmetric atom is present in the molecule. This has been shown to be correct

¹ *Voorstel tot Uitbreiding der Structuur-Formules in de Ruimte* (1874).

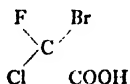
² *Bull. Soc. Chim.*, **22**, 337 (1874).

by the resolution of compounds containing an asymmetric nitrogen atom carried out by Pope,¹ Kipping,² H. O. Jones,³ Le Bel,⁴ Wedekind,⁵ and others. Pope and Kipping also confirmed these views by the resolution of compounds containing asymmetric sulphur,⁶ selenium,⁷ and tin atoms, and Kipping⁸ extended the work to compounds of silicon. Quinquevalent phosphorus compounds were successfully resolved by Meisenheimer and Lichtenstadt,⁹ and also by Kipping.¹⁰

The optical activity of such compounds has been ascribed to various causes. Guye¹¹ assumed that the different masses of the four univalent groups or atoms attached to the asymmetric atom was the chief factor. This was shown to be incorrect by the successful resolution of propyl-isopropyl-cyano acetic acid by Fischer and Flatau.¹²



In this compound two of the univalent groups are identical in mass; in spite of this the compound has a fairly high specific rotation. It was then suggested that the optical activity was due to the differences in chemical properties of the four atoms or groups. This again was shown to be incorrect by the work of Swarts,¹³ who resolved fluoro-chloro-bromo-acetic acid,



The optical activity of the compounds seems to be due to the asymmetric structure of the molecule alone, and later work under the leadership of Pope has fully confirmed this conclusion.

Van't Hoff and Le Bel in their theory laid down two conditions

¹ Pope and Peachy, *Chem. Soc. Trans.*, **75**, 1207 (1899); **79**, 828 (1901).

² Kipping, *Chem. Soc. Trans.*, **22**, 873 (1903).

³ *Chem. Soc. Trans.*, **83**, 1400 (1903).

⁴ *Compt. rend.*, **112**, 725 (1891).

⁵ Wedekind and Fröhlich, *Ber.*, **38**, 1838 (1905).

⁶ Pope and Peachy, *Chem. Soc. Trans.*, **77**, 1072 (1900); Smiles, *Chem. Soc. Trans.*, **77**, 1174 (1900).

⁷ Pope and Neville, *Chem. Soc. Trans.*, **81**, 107, 1552 (1902).

⁸ *Chem. Soc. Trans.*, **91**, 209, 717 (1907); **93**, 457 (1908).

⁹ *Ber.*, **44**, 356 (1911).

¹⁰ Kipping and Challenger, *Chem. Soc. Trans.*, **99**, 626 (1911).

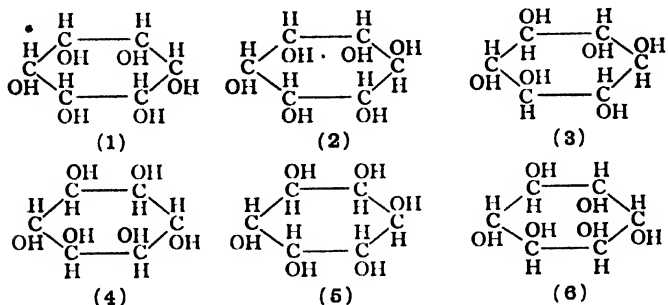
¹¹ *Compt. rend.*, **110**, 744 (1890); **116**, 1378 (1893).

¹² *Ber.*, **42**, 981 (1909).

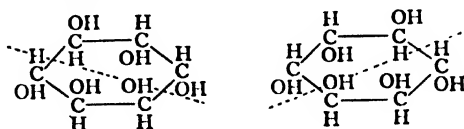
¹³ *Bull. Soc. Chim.*, **15**, 1134 (1896).

¹⁴ (D 340)

for the existence of optical activity: (1) an asymmetric structure of the molecule; (2) differences of groups surrounding the plurivalent atom. It will be seen that this second condition does not hold. In 1893, Maquenne¹ studied the inositols, i.e. the hexahydroxy-hexahydro derivatives of benzene, $C_6H_6(OH)_6$. Several isomers are possible in this case as is shown below, where the hydrogen and hydroxy groups are shown above or below the plane of the benzene ring.



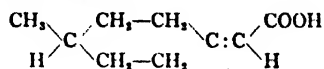
All these isomers except that represented by (6) possess a plane of symmetry, and are, therefore, superposable with their mirror images. Isomer (6), however, possesses no plane of symmetry, and is for this reason non-superposable with its mirror image, as is easily seen from the following figure:



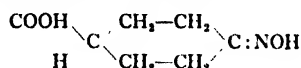
This molecule possesses a binary axis of symmetry, indicated in the figure by a dotted line, nevertheless the molecule is asymmetric. Asymmetry does not imply a complete lack of symmetry. Here we have a compound which contains no asymmetric carbon atom according to the van't Hoff-Le Bel theory, but which, nevertheless, was obtained in optically active forms by Maquenne. The dextro and laevo forms are non-superposable, and this seems to be the only condition necessary for optical activity. Further examples may be

¹ *Ann. de Chim. et Phys.*, **29**, 271 (1893).

found in the resolution of *l*-methyl-cyclohexylidene-4-acetic acid by Pope, Perkin, and Wallach:¹

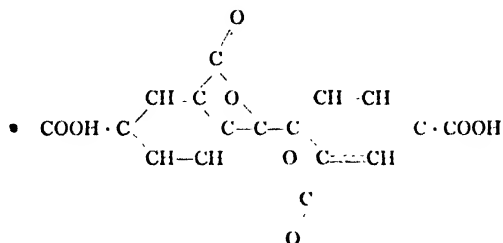


and of 4-oximino-cyclohexane carboxylic acid by Mills and Bain,²



The fact that Mills and Bain were able to obtain optical isomers of this compound proves that the molecule is asymmetric, and this necessitates an unsymmetrical situation of the NOH group with respect to the plane of the benzene ring. This supports Hantzsch's view of the configuration of the oximes.

Another recent example is the resolution of the keto-dilactone of benzophenone 2:4:2':4'-tetracarboxylic acid by Mills and Nodder.³



These optically active compounds show that the second condition laid down by van't Hoff and Le Bel is incorrect, i.e. the attachment of four different atoms or groups to the plurivalent atom is unnecessary, the asymmetric structure of the molecule being the one and only condition for the manifestation of optical activity.

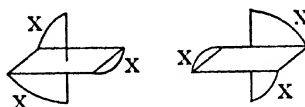
If we examine the structure assigned by Werner to the co-ordinated complexes of the type $[\text{MX}_3]$, where X occupies two co-ordinated positions, we find that the molecule possesses a fairly high degree of symmetry; it possesses a ternary axis and three hetero-polar axes of symmetry situated in a plane perpendicular to the X

¹ Chem. Soc. Trans., 95, 1789 (1909). ² Chem. Soc. Trans., 97, 1866 (1910).

³ Chem. Soc. Trans., 119, 2094 (1921).

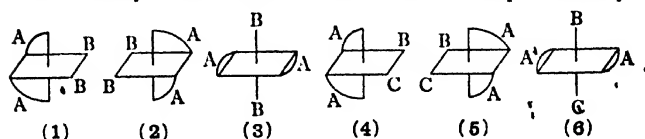
COMPLEX SALTS

groups. We find, however, that the molecule possesses neither a plane nor a centre of symmetry, and the molecule should therefore be non-superposable with its mirror image. This is shown in the accompanying figure, but should be verified by examining actual models.



Thus the molecule is asymmetric and the compound exhibits optical activity. The resolution of compounds of this type was accomplished by Werner in 1911. Here we have an excellent example of a molecule composed of even identical units, which possesses a fairly high symmetrical configuration, but can, nevertheless, be obtained in optically active forms because the molecule is asymmetric. The high rotatory power of these compounds is therefore due merely to the non-superposable arrangement as such, and not to any physical or chemical contrast of the groups around the central atom.¹ This conclusion has been stated by Pope in his presidential address to the chemical section of the British Association, 1914: "It must, however, be insisted that the observed optical activity is the result of the enantiomorphism of the molecular configuration; the asymmetry of a particular atom is not to be regarded as the cause of the optical activity but merely as a convenient geometrical sign of molecular enantiomorphism."

The co-ordinated complexes corresponding to the following types $[MA_2B_2]$ and $[MA_2BC]$ (A being a group occupying two co-ordinated positions, B and C occupying only one position) will on examination be found to be asymmetric, and should, therefore, exhibit optical activity.

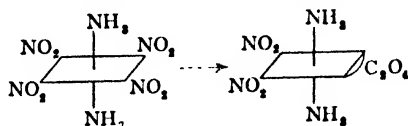


It may be noted here that the compound $[MA_2B_2]$ exists in two forms corresponding to the cis and trans configurations. (1) and (2) represent the non-superposable mirror images of the cis compound; (3) represents the trans isomer, which is seen to possess several planes of symmetry. The cis molecule being asymmetric should be resolv-

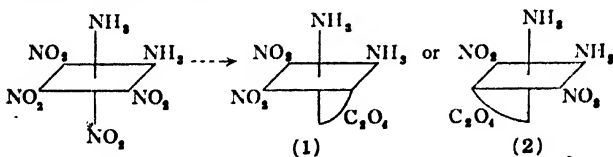
¹ Cf. Jaeger, *Principles of Symmetry*.

MOLECULAR ASYMMETRY AND OPTICAL ACTIVITY 53

able, and a large number of active compounds corresponding to this structure are known; the trans molecule, on the other hand, not being asymmetric, is non-resolvable. The same applies to the compound of the type $[MA_2BC]$; the cis-B-C compound is seen to have an asymmetric structure and is therefore resolvable (4) and (5), whereas the trans-B-C isomer has several planes of symmetry passing through the axis B-C (6). This may serve as a method of finding the structure of a compound of the above type, and has been applied by the author in the investigation of Erdmann's salt. This salt is ammonium tetranitro-diammine cobaltate, $[(NO_2)_4Co(NH_3)_2]NH_4$; it may have the cis- or trans-diammine structure. By the action of oxalic acid on this salt (details given in the chapter on preparations), two of the four nitro groups are replaced by an oxalato group; the products obtained will depend on the structure of Erdmann's salt. If this has a trans-diammine configuration, the product of replacement will be the oxalato-cis-dinitro-trans-diammine cobaltate,



If the tetranitro-diammine salt has the cis-diammine structure, then two products may be formed as shown below: (1) is oxalato-cis-dinitro-cis-diammine cobaltate, and (2) is the oxalato-trans-dinitro-cis-diammine cobaltate.

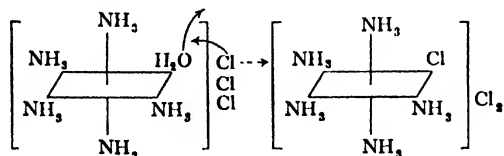


Of these products, the only complex with an asymmetric structure is the oxalato-cis-dinitro-cis-diammine cobaltate, all the others possessing a plane of symmetry. It has been found¹ that by replacing the two nitro groups by the oxalato radical two products were obtained, one of which was resolvable; hence Erdmann's salt is the cis-diammine complex.

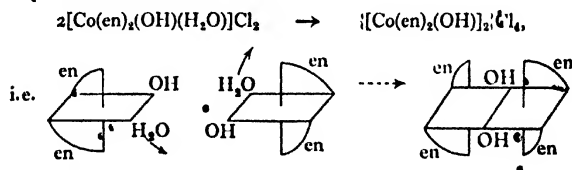
¹ Shibata and Maruki, *J. of the Coll. of Sci., Tokyo*, **41**, 1 (1917); Thomas, *Chem. Soc. Trans.*, **123**, 617 (1923).

The existence of optically active isomers among the complex salts was very strong evidence in favour of Werner's octahedral structure. Until 1914, all the complex salts which had been resolved contained carbon atoms, e.g. $[\text{Co}(\text{en})_3]$, and those who would not accept the octahedral arrangement pointed to the possibility of the optical activity being in some way bound up with the mode of linkage of these carbon atoms. To test this Werner¹ prepared a complex which contained no carbon atom, viz. hexol-dodecammine-tetracobaltic bromide, $[\text{Co}\{(\text{OH})_2\text{Co}(\text{NH}_3)_4\}_3]\text{Br}_6$, in which the complex $\{\text{Co}(\text{NH}_3)_4(\text{OH})_2\}$ plays the same rôle as ethylenediamine in the complex $[\text{Co}(\text{en})_3]$. He succeeded in resolving this compound, and found the active forms to have a molecular rotatory power of about 47600° .

This latter compound is an example of what may be termed a polynuclear complex, since the complex contains more than one central atom. The formation of such compounds will be readily understood from the following illustration. We have already seen that, if a compound containing a molecule of water in the complex is heated, the molecule of water is expelled and the character of the compound changes. Thus if we heat aquo-pentammine-cobaltic chloride we obtain as product chloro-pentammine-cobaltic chloride i.e. an acidic radicle enters the complex.



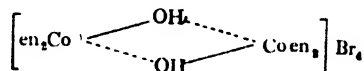
If, however, the complex contained a hydroxyl group as well as a molecule of water, then it is found that two complexes combine to form a new polynuclear complex, e.g.



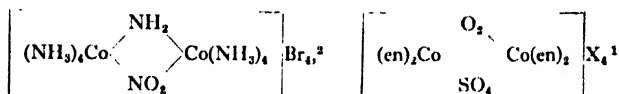
This also gives us the probable structure of the product. According

¹ *Ber.*, 47, 3087 (1914).

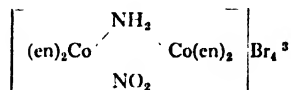
to the nomenclature of the complex salts, this product would be called tetra-ethylenediamine- μ -dihydroxy-dicobaltic chloride, the bridging position being denoted by μ . Werner¹ assumed that in this compound the oxygen atoms of the hydroxyl groups had a principal valency directed to one of the cobalt atoms and an auxiliary valency directed towards the other, thus:



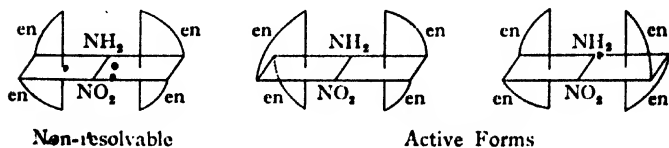
A large number of these polynuclear compounds are known, with the following among others as bridging groups: the imino group NH_2 , the peroxide group $-\text{O}-\text{O}-$, the nitro group NO_2 , and the sulphate radicle SO_4 ; e.g.



Among these polynuclear complexes Werner found the analogue of tartaric acid, where an internally as well as an externally compensated compound is possible. Thus tetraethylenediamino- μ -nitro- μ -imino- μ -cobaltic bromide,



gives the dextro, lævo, racemic, and the meso or the internally compensated compound.



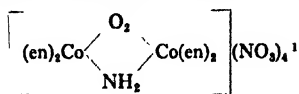
It is seen that the non-resolvable complex has a plane of symmetry passing through the amino and the nitro groups. Tetraethylene-

¹Werner, *Ann.*, 375, 1 (1910).

²Werner, *Ber.*, 46, 3674 (1913).

³Werner, *Ann.*, 375, 1 (1910).

diamine- μ -peroxo- μ -monimino-dicobaltic nitrate is another example:



The configurations of the meso and the active forms are analogous to those given above. It might be mentioned that this complex has the highest molecular rotatory power of any known active compound, $[\text{M}]_D^{25} = 68550^\circ$, $[\text{M}]$ being calculated as given in Chapter VII.

It may not be out of place here to review very briefly the isomers obtained by Werner² with propylenediamine in the complex. This amine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{NH}_2$, contains an asymmetric carbon atom and can therefore exist in three isomeric forms, dextro, lævo, and the racemic form. The possible complexes are $[\text{Co}(\text{dpn})_3]\text{Cl}_3$, $[\text{Co}(\text{lpn})_3]\text{Cl}_3$, $[\text{Co}(\text{dpn})_2(\text{lpn})]\text{Cl}_3$, and $[\text{Co}(\text{dpn})(\text{lpn})_2]\text{Cl}_3$. Each one of these should be resolvable and hence exist in three forms; thus twelve compounds are possible. Werner started with the three isomeric amines and was able to isolate each one of the twelve isomers.

¹ Werner, *Ber.*, **47**, 1961 (1914). ² *Helv. Chim. Acta*, **1**, 5 (1917).

CHAPTER VI

Methods of Resolution

It is to Pasteur that we are indebted for the general methods now in use for the resolution of racemic compounds into their optically active isomerides. These will be briefly considered and their application to the resolution of inorganic complex salts discussed.

Separation by Spontaneous Crystallization.—Pasteur¹ crystallized a solution of sodium ammonium racemate at ordinary temperatures, and discovered that the crystals deposited exhibited hemihedral facets, and were enantiomorphous. He separated these crystals into two heaps according to the position of the facets, and found that a solution of the one heap rotated the plane of polarization of polarized light in the one direction while that of the other rotated it in the opposite direction, i.e. Pasteur separated the compound into its optical isomers. Scacchi² repeated this experiment and found that if the crystallization is carried above 27.2° C. no enantiomorphous crystals are deposited, but holohedral crystals of sodium ammonium racemate. Below 27.2° C., Scacchi obtained the same results as Pasteur. It was later shown by van't Hoff that the spontaneous separation by crystallization is analogous to the formation and decomposition of double salts. In the case of sodium ammonium racemate, 27.2° C. is the transition temperature for the change



Above 27.2°C. the racemate is the stable phase and consequently the less soluble, hence crystallization above this temperature deposits the racemate. Below the transition temperature the active forms are the more stable and the less soluble, therefore a saturated solution kept below this temperature will gradually deposit crystals of the active components. If the solution is kept at the transition temperature, the crystals deposited will be a mixture of the racemate and the

¹ *Compt. rend.*, 26, 535; 27, 101, 367 (1848); *Ann. de Chim. et Phys.*, 24, 442, 1848). ² *Rendic. dell' Acad. di Napoli*, 250 (1865).

curve *acb* consists of two branches, *ac* and *bc*, which represent the composition of the solution in contact with the dextro and laevo components respectively as solid phases. At the point represented by *c* the solution is saturated with both forms; this point lies on the bisector of the angle *bOa*, since the isomers have the same solubility. At t_1 , the racemate (the metastable solid phase) has a higher solubility than a mixture of the active forms; its solution will therefore deposit crystals of the active components, i.e. resolution by spontaneous crystallization occurs. We will now consider a temperature t_2° , which is below the transition temperature. The solubilities of the active forms are given by *de* and *lg*; in this case the two curves do not meet, but are joined by the curve *efg*, which refers to the racemic compound. The solubility of the racemate is represented by the point *f*. By the addition of the dextro or the laevo form to this saturated solution of the racemate, the composition of the solution changes from *f* to *e* or *f* to *g* respectively. The point *e* thus represents a solution in equilibrium with the racemate and the dextro salts as solid phases, *g* being the corresponding point for the racemate and the laevo compounds. The racemate, being at this temperature the stable solid phase, has a lower solubility (*f*) than the metastable mixture of the active salts, which is represented by *k*, the point of intersection of the curves *de* and *lg*. As the temperature approaches the transition temperature, the points *g* and *e* approach (they lie on the branches AE and AC). At the transition temperature (A) they meet, i.e. the solution can now be in equilibrium with the racemate and the active forms. If the racemate is the stable form at the higher temperature and the active forms at the lower temperatures, then the curves are represented in fig. 3. The different cases should be worked out by the student. These curves are analogous to those given for the formation and decomposition of double salts. In the case of the racemates, the solubilities of the components are equal and hence the curves are symmetrical, whereas this is not generally the case with double salts (cf. fig. 3). (Cf. Findlay's Phase Rule.)

In the case of complex salts, only one case is so far known of separation by spontaneous crystallization; this is in the case of potassium cobalti-oxalate, $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{K}_3$, which was investigated by Jaeger and Thomas.¹ On crystallization of the racemate at temperatures above 13.2°C ., crystals of the active forms were deposited, whereas below this temperature the racemate separated

¹ *Proceed. Kon. Akad. v. Wet.*, 21, 702 (1918); *Rec. des Trav. Chim. des Pays-Bas*, 38, 171 (1919).

out. The transition temperature was found by the solubility method, i.e. the determination of the temperature at which the solubilities of the racemic and active forms are equal (cf. Findlay's Phase Rule). Below 13.2°C . the racemate had the lower solubility and was therefore the stable phase in contact with the solution, whereas above 13.2°C . the active forms were the less soluble and were consequently the

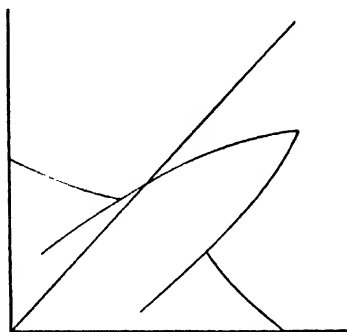


Fig. 3

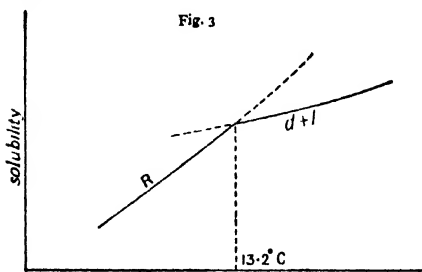
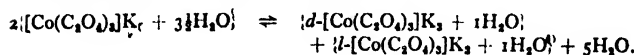


Fig. 4

stable solid phase, cf. fig. 4. The racemic potassium cobalti-oxalate contains $3\frac{1}{2}$ molecules of water of crystallization, whereas the active forms contain one molecule.

Thus at 13.2°C . we have the equilibrium



Separation by Combination with an Active Molecule.—

This is by far the most important method of resolution and was also

discovered by Pasteur.¹ If a solution of racemic acid is combined with the equivalent of cinchonine and a solution of the salt obtained crystallized, the first crop of crystals is found to consist of the cinchonine salt of lævotartaric acid, while the corresponding salt of the dextro acid remains in solution, being therefore the more soluble. It has already been stated that the solubilities of optical isomers are equal, which holds in the case of the free acid and in the case of its salts. Fractional crystallization of the cinchonine salt has, however, resulted in a resolution, this being made possible by a difference in the solubilities of the dextro and the lævo salts. This does not in any way contradict the above statement, because the cinchonine salts are not optical antipodes. Suppose we are dealing with a racemic acid, which we can represent by dA/A , i.e. a compound of the dextro and the lævo forms. On crystallizing a solution of this, the crystals will be either the racemate or a conglomerate of the active forms; the mother liquor will always contain the d and l forms in equivalent amounts, because the solubilities of these isomers are equal. The racemate is now combined with an active base, which we can denote by dB ; two compounds are formed, $dBdA$ and $dBIA$. The mirror image of $dBdA$ is $IBIA$ and not $dBIA$, the other product of the above reaction; hence the products of the combination of a racemic acid with an active base are not mirror images, i.e. they are not optical isomers. Their physical properties will then, in general, be different. If their solubilities are different, then a separation can be effected by subjecting the solution of the products to fractional crystallization. The salts so obtained are then decomposed to give the free active acids. In addition to cinchonine, the other active alkaloids have been employed successfully in the resolution of racemic acids. In the same way, a racemic base can be resolved by combination with an active acid, the active acids generally employed being tartaric acid and its derivatives, nitro-camphor, and camphor-sulphonic acid.

This method of resolution has been applied with very great success to the resolution of inorganic complex salts. Thus Werner² in 1911 succeeded in obtaining the active forms of $[\text{Co}(\text{en})_3]\text{Br}_3$, $[\text{Cr}(\text{en})_3]\text{Cl}_3$, $[\text{Ir}(\text{en})_3]\text{Br}_3$, &c., by combination with active acids. The active acids employed were d -bromo-tartaric acid and the acid derivatives of camphor, Werner's first attempts by combination with active tartaric acid being unsuccessful. Later, a large number of compounds with complex anions were resolved, e.g. the complex oxalates of cobalt, chromium, iridium, rhodium, and iron, the complex

¹ *pt. rend.*, 36, 191 (1852).

² *Ber.*, 45, 121 (1911).

malonate of iridium, &c. In most cases, the alkaloids were employed as active bases. It was noted above that the first attempts of Werner to resolve the complex salts by combination with active tartaric acid were not successful. The necessary conditions for a successful resolution by this method are:

1. Stability of the intermediate compound.
2. Favourable solubility relationship.

The importance of these conditions is well illustrated in the case of potassium ferri-oxalate.¹ Efforts were made to effect a resolution by combination with an alkaloid, but on crystallization the alkaloid salt of the complex ferrous oxalate was obtained. Evidently the intermediate compound is here unstable, and resolution by fractional crystallization of the alkaloid salt was thereby rendered impossible. To avoid this decomposition, the method of fractional precipitation was substituted for fractional crystallization—again without success, indicating that the solubility relationship is also unfavourable. The salt was successfully resolved by combination with α -phenylethylamine as the active base, $C_6H_5CH(NH_2)CH_3$, the salt of this active base with the complex being stable and the solubility relationship suitable.

Another difficulty experienced in attempts to resolve by this method is the formation of a partially racemic compound; i.e. the base in the above case, for example, may combine with the whole of the racemic compound as such, and not directly with each of the active forms. To follow the solubility relationship in such cases, the reader should consult works on the phase rule.

A slightly modified form of this method of resolution was discovered by Werner.² This will best be made clear by reference to its application. To a saturated solution of racemic $[Co(en)_2(NO_3)_4]Br$ (dinitro - diethylenediamine - cobaltic bromide) were added some crystals of dextro - oxalato - diethylenediamine - cobaltic bromide, $[Co(en)_2C_2O_4]Br$, alcohol being then added until some of the salt was precipitated. It was found that the dinitro salt precipitated was dextrorotatory, whilst the mother liquor became levorotatory. This modification was also applied with success to the resolution of the corresponding oxalato complex of chromium, $[Cr(en)_2C_2O_4]Br$, but failed in the case of the dichloro derivative, $[Cr(en)_2Cl_2]Cl$. The added active form must be isomorphous with one of the active

¹ Thomas, *Chem. Soc. Trans.*, 119, 1140 (1921).

² *Ber.*, 47, 1955, 2171, 2179 (1914).

forms of the racemate, for it appears that the added crystals act as nuclei for the separation of the one active form.

Separation by Living Organisms.—The third method of resolution employed by Pasteur consists in subjecting a solution of the racemate to the action of some of the lower plant organisms, e.g. moulds, bacteria, &c. In the case of ammonium racemate, for example, the introduction of the green mould *Penicillium glaucum* to the solution results in the solution becoming levorotatory. The mould grows in the solution and destroys the salt of the dextro acid. The one active component can thus be obtained. This method has not, however, been applied with success to the resolution of complex salts.

CHAPTER VII

Characteristics of Optically Active Complex Salts

Anomalous Rotation.—It is well known that the magnitude of the specific or molecular rotatory power of an active compound depends on the wave-length of light employed. It is, therefore, necessary in determining these values to work with monochromatic light. Jaeger and his research workers have investigated the dispersion curves of several of these compounds, and their results will be briefly discussed.

In fig. 5 are given the dispersion curves of some of the triethylenediamine salts of cobalt.¹ These may be compared with the corresponding curve for cane-sugar. In the curves the molecular rotation is plotted against the wave-length of light. The molecular rotatory power has been calculated by means of the formula

$$[M] = \alpha \frac{V}{l},$$

where α is the observed angle of rotation, l is the length of the tube in centimetres, and V is the volume of the solution in cubic centimetres containing a gramme-molecule of the active substance. Solutions of these complex salts are generally very intensely coloured, and in certain cases very dilute solutions had to be employed for taking the measurements. The figure shows that the molecular rotatory power of the complex triethylenediamine salts of cobalt for red light is almost the same as that for cane-sugar, but for shorter wave-lengths the rotation of the complex cobaltic salts is very much the greater. It is also seen that the values for the chloride, bromide, iodide, nitrate,

¹ Jaeger, *Proceed. Kon. Akad. v. Wet.*, **17**, 1231 (1915); *Rec. des Trav. Chim. des Pays-Bas*, **38**, 171 (1919).

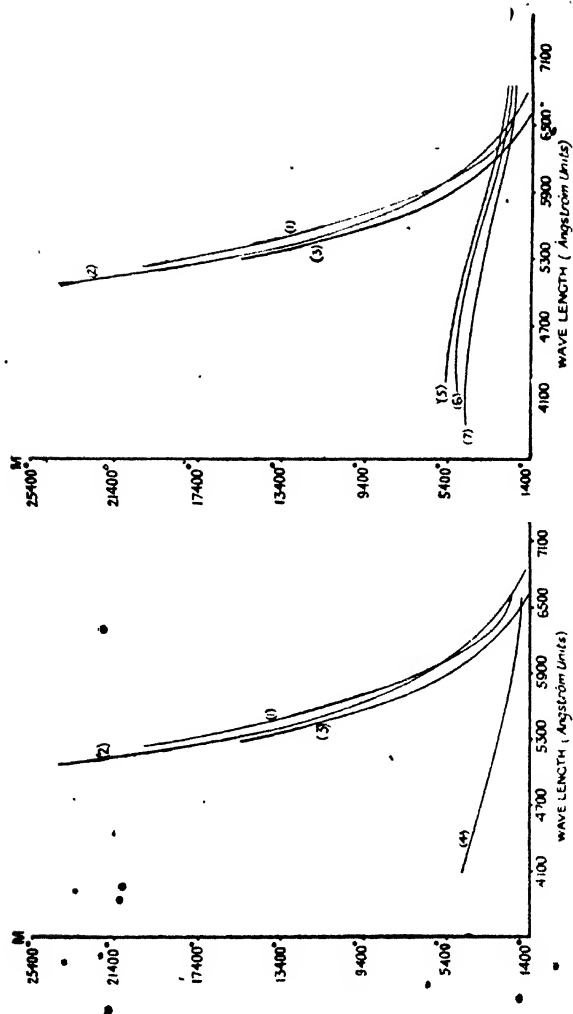


Fig. 5

1. Triethylenediamine Cobaltic Iodide
2. " " " Bromide
3. " " " Nitrate

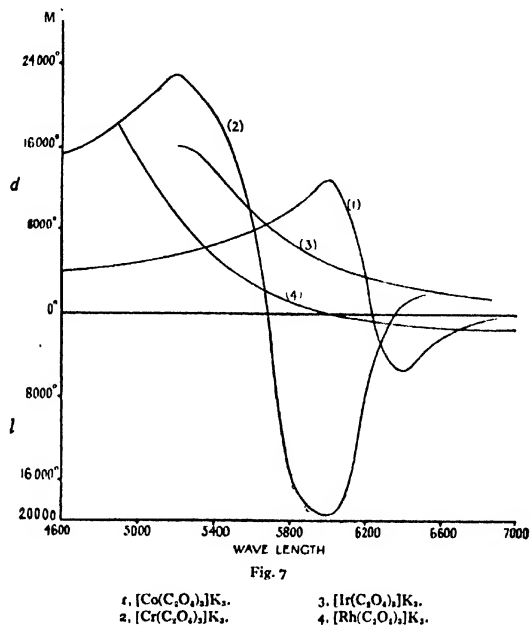
Fig. 6

5. Triethylenediamine Rhodium Nitrate
6. " " " Bromide
7. " " " Iodide

&c., of the triethylenediamine-cobaltic complex follow one another very closely, indicating that the nature of the dispersion curve is chiefly dependent on the complex. The influence of the central

(D 340 f)

atom is brought out very clearly by reference to fig. 6, where the dispersion curves of the triethylenediamine complex salts of cobalt¹ and rhodium are plotted. The curves for the corresponding complex salts of chromium run almost parallel with those of cobalt. The colours of the cobalt and chromium series are much more intense than the corresponding complexes of rhodium. Jaeger suggests that the colour of the solution has a very great influence



on the form of the dispersion curve. The relationship between colour and dispersion curve is made more manifest in the curves for the complex oxalates of cobalt, chromium, rhodium, and iridium, which are represented in fig. 7. Here again a similarity is observed in the curves of the cobaltic and chromic complexes on the one hand, and between the rhodium and iridium complexes on the other hand. The rotatory power of the iridium complex decreases gradually with

¹ Jaeger, *Proceed. Kon. Akad. v. Wet.*, 17, 1231 (1915); *Rec. des Trav. Chim. des Pays-Bas*, 38, 171 (1919). ² *Ibid.*

increasing wave-length of light. The same applies to the active rhodium complex, but in this case the rotation becomes zero for light of wave-length 6000 Årgström units, i.e. for light of this particular wave-length potassium rhodium oxalate is inactive, and for light of longer wave-length the rotation is in the other direction. It is thus seen that the direction of rotation as well as its magnitude depends on the wave-length of light employed.

It will be interesting and instructive to consider in more detail

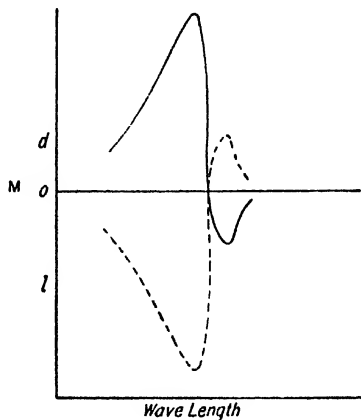


Fig. 8

the dispersion curve of the active potassium cobalti-oxalate. The curve is represented in fig. 8, the dotted line representing the dispersion curve of the antipode (the curves for the active isomers are, of course, mirror images). Here again we have a compound which is dextrorotatory, inactive, or levorotatory according to the wave-length of light employed. The curve for this compound is, however, more complicated than for the rhodium complex, the curve here exhibiting a maximum and a minimum. In the cases cited, the rotatory power was measured by means of a Haentzsch-Schmidt polarimeter. A Nernst lamp was employed as a source of light, and a spectrum obtained by passing the light through a prism. Very narrow sections of this spectrum were admitted by means of a narrow slit; the light thus employed was not purely monochromatic and this probably influenced the results. Measurements carried out with monochromatic light would probably give the curves repre

sented in fig. 9. Here the dispersion is represented by two curves, which would show an infinite rotatory power at a wave-length of 6200 Ångström units. Drude's formula would probably be applicable to these curves, as has been found by Lowry¹ in the case of a large number of organic compounds.

A solution of potassium cobalti-oxalate shows a strong absorption band at a wave-length corresponding to the maximum and the

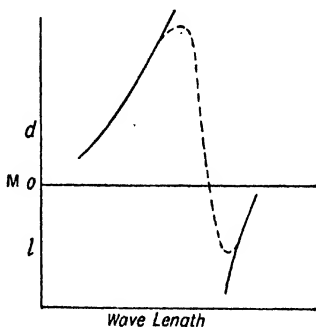
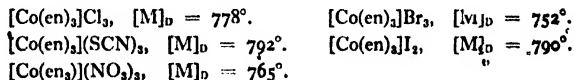


Fig. 9

minimum in the curve. This supports the suggestion of J that the colour has a great influence on the form of the dispersion curve.

Rotatory Power and Constitution.—Very little is yet known of the relationship between the magnitude of the rotatory power and the constitution of the active compounds. It has been found that in the case of the complex salts the group outside the complex has but little influence,² e.g.

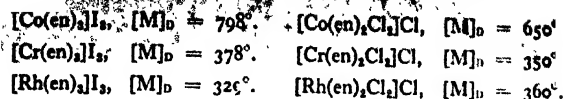


The central atom has, however, a marked influence on the magnitude of the rotation, as can be seen from the following results:³

¹ Lowry and Cutter, *Chem. Soc. Trans.*, 121, 532 (1922); Lowry, *ibid.*, 103, 667 (1913).

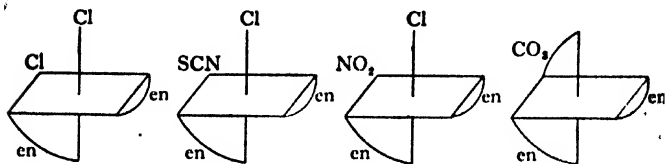
² Werner, *Ber.*, 45, 2134, 1236 (1912); *loc. cit.*

³ *ibid.*

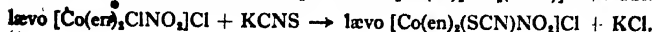
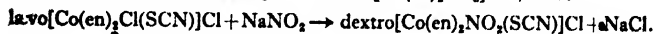


Whereas chromium and rhodium complexes have approximately the same rotatory power, the values for the corresponding cobalt compounds are much higher. This is unexpected in view of the fact that the atomic weight of rhodium is almost twice that of chromium.

Optical Activity and Configuration.—A large number of compounds of the type $[\text{Co}(\text{en})_2\text{XY}]$ have been resolved, and it is interesting to investigate whether compounds of similar configuration will rotate the plane of polarized light in the same direction, i.e. the question arises, will the following molecules rotate the light in the same direction?

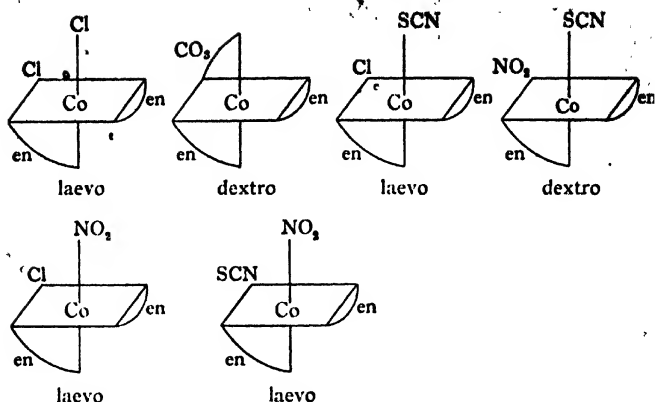


These represent similar configurations of the antipodes, and Werner,¹ by carrying out a series of transformations, attempted to find the relation between the direction of rotation and the configuration. He submitted *laevo*-dichloro-diethylenediamine-cobaltic chloride to the action of potassium carbonate, sodium nitrite, &c., and examined the carbonate, nitro, &c., products to see whether the direction of rotation had been changed. His results were as follows:

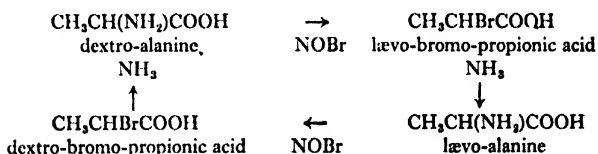


In two of these cases we find a change in the direction of the rotation. Werner now assumed that no molecular transformation occurred during the reaction, and that the products formed were of the same configuration as the initial complex. On these assumptions the above results can be expressed as follows:

¹ *Ber.*, 45, 1229 (1912).



i.e. molecules having the same configuration and the same central atom show rotations in opposite directions. It is, however, well known that a change of configuration often occurs during a substitution, as is well exemplified by the Walden inversion. Walden carried out the following substitutions, and obtained the results shown in the table:

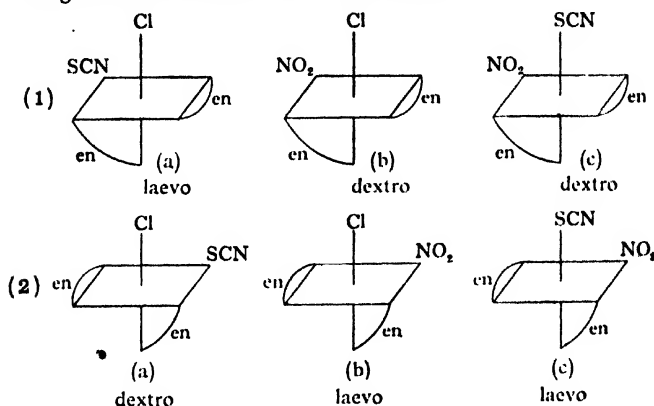


In this cycle one starts with dextro-alanine and passes through the laevo antipode, obtaining finally the dextro-amino acid. It is evident that a change of configuration has occurred during these transformations. Hence it is not correct to assume that in a chemical reaction in which one radicle is displaced by another the group introduced takes the place of the radicle removed. Examples of such changes in configuration in the case of inorganic complex salts have already been given in Chapter III.

The above conclusions of Werner cannot be considered proved by these transformations. In the results of resolution, however, Werner¹ believes that he has obtained further evidence in favour of

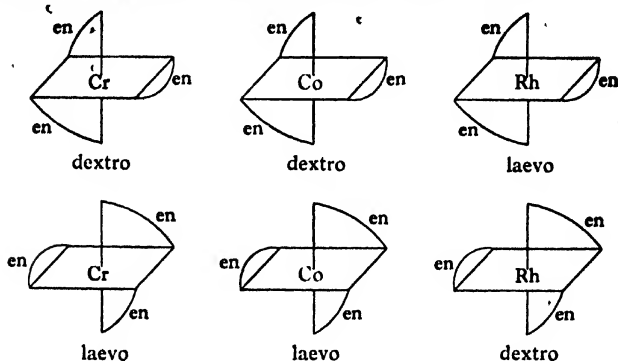
¹ Ber., 45, 1229 (1912).

the above. The compounds $[\text{Co}(\text{en})_2\text{Cl}(\text{SCN})]\text{Cl}$, $[\text{Co}(\text{en})_2\text{Cl}(\text{NO}_2)]\text{Cl}$, and $[\text{Co}(\text{en})_2\text{NO}_2(\text{SCN})]\text{Cl}$ were resolved by combination with dextro-brom-camphor sulphonic acid and fractional crystallization of the salts formed. The first fractions were in each case decomposed to give the active complex, and the following active components were obtained: lævo- $[\text{Co}(\text{en})_2\text{Cl}(\text{SCN})]\text{Cl}$, dextro- $[\text{Co}(\text{en})_2\text{Cl}(\text{NO}_2)]\text{Cl}$, and dextro- $[\text{Co}(\text{en})_2(\text{NO}_2)(\text{SCN})]\text{Cl}$. Werner claimed that the complexes with analogous structure form in each case the less soluble salt with the active acid, i.e. the active complexes with the same configuration are obtained in the first fractions:



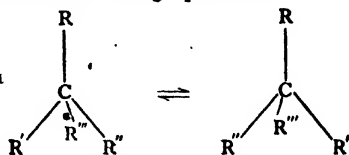
These conclusions are summarized in the above table. Compounds (1) are thus assumed to have the same configuration and to have the rotations as given; the same would then naturally apply to their antipodes, which are represented in (2). It is seen that these results agree with those obtained by the substitution experiments. Encouraged by this agreement, Werner generalizes and states that, in all cases of resolutions, complexes of similar configuration form the less soluble salt with the active base or acid employed for the resolution. The triethylenediamine complexes of cobalt, chromium, and rhodium* may be cited as further examples, these basic complexes being resolvable by combination with camphor sulphonic acid as the active acid. If the dextro acid is employed the first fractions contain the dextro-, dextro-, and lævo-complexes of chromium, cobalt, and rhodium respectively. Hence from the above assumptions these active forms have the same configuration. Assuming that

the chromium complex has the configuration given, we can then give the configuration of the other active compounds, e.g.



According to this, chromium and cobalt complexes of similar configuration possess optical activity of the same sign, whereas the corresponding rhodium complex has a rotatory power of the opposite sign. Further evidence is necessary before these conclusions can be accepted, but they have been discussed because they are very interesting and may suggest to the reader a very fascinating subject of research.

Racemization.—When van't Hoff and Le Bel¹ advanced the tetrahedral theory for the structure of organic compounds, they pointed out that the groups were not supposed to be fixed at the corners of a regular tetrahedron, but that these merely represented their mean positions of oscillation. The atoms or groups attached to a carbon atom are thus imagined to be in a state of vibration, an assumption which enables us to understand such phenomena as racemization, tautomerism, &c. If an active compound $CRR'R''$, for example, loses its activity, one-half of the molecules must have undergone molecular transformation to produce its antipode, and there is in solution the following equilibrium:

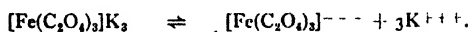


¹ Van't Hoff, loc. cit.; Le Bel, loc. cit.

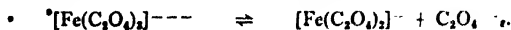
When racemization is complete, i.e. when the solution is inactive, the antipodes are present in solution in equal amounts because they have equal but opposite rotatory powers. As the temperature increases, it is natural to assume that the amplitude of the vibrations of the atoms or groups also increases; this would result in an increase in the rate of racemization. This is in full agreement with experimental results. In the case of organic compounds, therefore, the cause of racemization is regarded to be the vibrations of the atoms or groups around the central atom.

In the field of inorganic complex salts, this phenomenon of racemization was first observed by Werner.¹ He noticed that a solution of active tripyridyl ferrous chloride, $[\text{Fe}(\text{pyr})_3]\text{Cl}_2$, rapidly lost its activity; the same was observed later in the case of potassium chromioxalate,² $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{K}_3$.

The racemization of the complex oxalate was more closely investigated by Rideal and Thomas.³ The temperature coefficient was found to be 1.75 for a rise of 10°C .; it was found that the dry salt could be heated to 90°C . without undergoing racemization. The addition of acetone to the solvent greatly retarded the rate of racemization. Another example of this phenomenon among the inorganic complexes was found by Thomas,⁴ who carried out the resolution of potassium ferri-oxalate, $[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{K}_3$; the active components of this complex lose their activity very rapidly, the rotatory power being reduced to one-half of its original value in fifteen minutes. This led the author to suggest a new theory of racemization in the case of these complex electrolytes. The above formulation for the complex ferri-oxalate suggests that in aqueous solution ionic dissociation occurs as follows:



It will be seen in a later chapter that these complex ions vary to a very large extent in their stability. The complex ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{---}$ is an unstable ion, and undergoes secondary ionization; this can be represented as follows:



This new complex ion contains four co-ordinating points, and in such compounds the four points lie in one plane. The oxalate ion

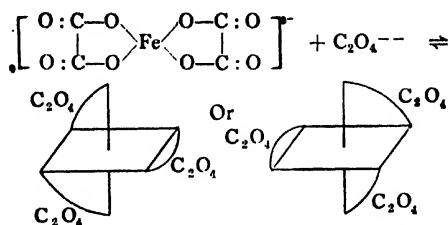
¹ *Ber.*, 45, 434 (1912).

² *Werner, Ber.*, 45, 3065 (1912).

³ *Chem. Soc. Trans.*, 121, 196 (1922).

⁴ *Chem. Soc. Trans.*, 119, 1140 (1921).

could then re-enter the complex in two ways to form either of the antipodes.



This theory is supported by the fact that the addition of acetone to an aqueous solution of potassium chromi-oxalate retards the rate of racemization, the effect being probably due to the reduction in ionization. Recent measurements¹ of the concentration of oxalate ions are in agreement with these views.

Optical Activity and Crystalline Form.—We have already seen that there is a connection between molecular asymmetry and optical activity, both in the case of carbon compounds and in the case of complex salts. Pasteur further postulated that an asymmetric molecule will produce enantiomorphous crystals. This has been tested in a very large number of cases, more especially in the field of organic chemistry. A large number of crystals of optical isomers were found to exhibit no hemihedral facets, but careful re-examination of these so-called exceptions to Pasteur's second law resulted in many cases in the detection of enantiomorphous forms. It may be said that the more delicate the method of detecting hemihedrism becomes, the more often is Pasteur's law found to be obeyed. Some exceptions, however, still remain; no indication of hemihedrism was found in lupeol, which was examined by Jaeger,² nor in tetrahydro-quinaldine hydrochloride, which was examined by Pope and Peachey,³ the corrosion method of investigation being employed in both researches.

Up to quite recently the compounds examined were those containing an asymmetric carbon atom. The researches of the last twenty-five years, however, have revealed optical activity in a large number of compounds with other elements as central atoms, a fact which has extended the scope of applicability of Pasteur's second law. Jaeger⁴

¹ Thomas and Fraser, *Chem. Soc. Trans.*, **124**, 2973 (1923).

² *Zeit. f. Kryst. u. Miner.*, **44**, 568 (1908). ³ *Chem. Soc. Trans.*, **75**, 1066 (1899).

⁴ *Rec. des Trav. Chim. des Pays-Bas*, **38**, 171 (1919).

extended his crystallographic researches to the optically active inorganic complex salts. These offer a good field for investigating the influence of the different factors on the development of hemihedral facets. In carbon compounds there are two factors: (1) the asymmetry of the molecule, (2) the different groups or atoms surrounding the carbon atom. If, now, compounds of the type $[M(Y)_3]X_3$ are examined, the influence of the asymmetry of the molecule can be ascertained. With this in view, Jaeger examined compounds of the type $[M(en)_3]X_3$. These compounds possess a very high rotatory power, but enantiomorphism, though detectable in many cases, is very feebly developed. The same results were obtained with compounds containing a complex anion, e.g. $[Co(C_2O_4)_3]K_3$. These results show very clearly that there is no relationship between magnitude of rotatory power and the tendency to develop hemihedrism. Jaeger concluded that while optical activity appears to be chiefly caused by the non-superposable atomic arrangement, the enantiomorphism seem to be more generally influenced by chemical contrast of the atoms or groups around the central atom. This was not, however, supported by the results of an investigation carried out by Thomas, who resolved ammonium oxalato-cis-dinitro-cis-diammine cobaltate, $[Co(NO_2)_2(NH_3)_2(C_2O_4)]NH_4$, no hemihedrism being detected in the crystals of the active isomers.

It must be remembered that many substances will develop this hemihedrism only under special conditions; under other conditions it may remain latent. Calcium malate when crystallized from water shows no hemihedral facets, but, if a little nitric acid is added to the saturated solution, enantiomorphous crystals are obtained. Again, Pasteur¹ found that active ammonium malate crystallized from water gave holohedral crystals, but that on cooling the fused salt hemihedral crystals were obtained.

¹ *Jahresber. f. Chem.*, 176 (1852).

CHAPTER VIII

Compounds with Co-ordination Number Four

The complex salts so far discussed have had a co-ordination number equal to six; those with co-ordination number higher than six are very rare, but a very large number of complex compounds are known with a value lower than six. The most common are those with co-ordination number equal to four. It will be seen that the methods of study are analogous to those employed in the case of the hexammines and their derivatives.

CO-ORDINATION NUMBER EQUAL TO FOUR

The Tetrammine Group.—Compounds of this class are most common with a bivalent metal as the central atom. Hexachloroplatinic acid, $[\text{PtCl}_6]\text{H}_2$, gives platinous chloride on being heated to 300°C .: $[\text{PtCl}_6]\text{H}_2 \rightarrow \text{PtCl}_2$. If ammonia is allowed to react on this salt, a product is obtained whose composition corresponds to $\text{PtCl}_2 \cdot 4\text{NH}_3$.¹ This compound dissolves in water; the aqueous solution reacts with silver nitrate, giving a precipitate of silver chloride; a quantitative estimation shows that both the chlorine atoms are so precipitated. Concentrated sulphuric acid reacts to form hydrochloric acid, and the corresponding sulphate remains. During these reactions the four ammonia molecules remain intact. The addition of alkali does not produce a precipitate of the hydroxide of platinum in the cold; this is, however, produced on warming; the same applies to the expulsion of ammonia. The molecular conductivity corresponds approximately to the value for ternary electrolytes, $\mu_{1000} = 267$ (BaCl_2 , $\mu_{1000} = 270$). Cryoscopic determinations of the molecular weight also indicate dissection into three ions. The three ions

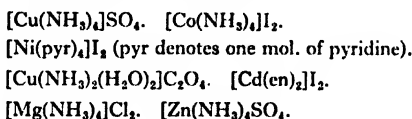
¹ Reiset, *Compt. rend.*, 11, 711 (1840).

COORDINATION NUMBER EQUAL TO FOUR. 77

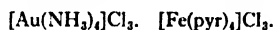
consist of two chlorine anions and a complex cation containing the platinum atom and the four ammonia molecules.¹ Hence the compound receives the following formulation:



In dealing with the hexammines, it was found that the ammonia molecules could be replaced by a number of other molecules to form a variety of compounds; those other molecules generally contained the atoms nitrogen, oxygen, or sulphur, i.e. they contained atoms which possessed residual valency. The same applies to these compounds with co-ordination number equal to four. Analogous complexes are also formed with other bivalent metals in the place of platinum, e.g. cobalt, nickel, copper, cadmium, zinc, magnesium, mercury, &c. Thus a large number of compounds of the above type are known; the following may be given as examples:

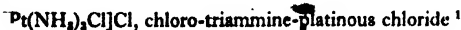


Tetrammine compounds have also been prepared with a tervalent central atom, e.g.



Since in these compounds no negative groups are found in the first sphere, the valency of the central atom is given by the number of negative groups outside this first sphere.

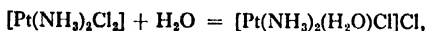
Monacido-triammine Group.—In tetrammine platinous chloride, four ammonia molecules are found in the first sphere. The expulsion of one of these molecules would leave a vacant co-ordination point in the first sphere; an acidic radicle would then enter the complex. If, for example, tetrammine-platinous chloride is heated with hydrochloric acid under pressure, a product is obtained having the composition $\text{PtCl}_2 \cdot 3\text{NH}_3$. The usual tests indicate that this compound dissociates in aqueous solution, giving a chloride anion and a complex cation containing one platinum atom, three molecules of ammonia, and a chlorine atom, i.e. it is a binary electrolyte, $\mu_{1000} = 116$ (NaCl , $\mu_{1000} = 118$). The compound is thus given the co-ordination formula



¹ Peyrone, *Ann.*, 51, 1; 55, 205; 61, 178 (1847).

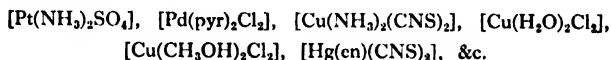
Of the few compounds of this type which have been prepared, the following is well known: $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}]\text{Cl} + \text{H}_2\text{O}$,¹ chloro-triaquachromium chloride with one molecule of water of crystallization.

Diacido-diammine Group.—If a second molecule of ammonia leaves the co-ordinated complex, then the second acidic radical enters, giving a diacido derivative. The product from the chlorotriammine platinumous chloride would thus be dichloro-diammine platinum, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. This compound can be obtained by heating dry tetrammine platinumous chloride to 250°C . (Reiset²) or by evaporating it with concentrated hydrochloric acid (Peyrone³). The central atom in this compound is bivalent and two groups are found in the co-ordinated complex, hence the valency of the complex is zero. It is readily seen that the complex is a non-electrolyte analogous to the triacido-triammine compounds described in Chapter II. If an aqueous solution is kept for some time it becomes a conductor of electricity (cf. the triacido-triammine compounds). This change can be represented as follows:



i.e. a molecule of water enters the first sphere, and an acidic radical leaves the complex and becomes ionic. The rate of this change can be found by measuring the rate of increase of the conductivity. The rate of hydration increases very rapidly with the temperature.

A large number of compounds belonging to the diacido-diammine type are known, e.g.

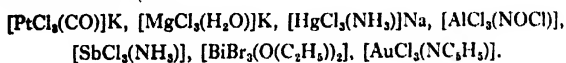


Triacido-monammine Group.—If the calculated amount of ammonia is allowed to react on potassium tetrachloro-platinite, a product is obtained with the composition $\text{PtCl}_3\text{NH}_3\text{K}$. A cold aqueous solution of this compound gives the analytical reactions of potassium, but not of the other atoms or groups present, indicating that they are present in a complex ion. The molecular conductivity at a thousand litres dilution has a value equal to 110, which is that of a binary electrolyte (cf. NaCl , $\mu_{1000} = 118$). The compound thus receives the formula $[\text{Pt}(\text{NH}_3)\text{Cl}_3]\text{K}$, potassium trichloro-monam-

¹ Knight and Rich, *Chem. Soc. Trans.*, 99, 87 (1911).

² Dammer, *Handb. d. anorg. Chem.*, 3, 815.

mine platinite. The complex in this case exists in aqueous solution as a complex anion, and is univalent. The principal valencies of two chlorine atoms in the complex are satisfied by the bivalent central platinum atom, the principal valency of the third chlorine atom being satisfied by a positive group outside the complex, in the above case the potassium atom. The following may be given as further examples of this type:

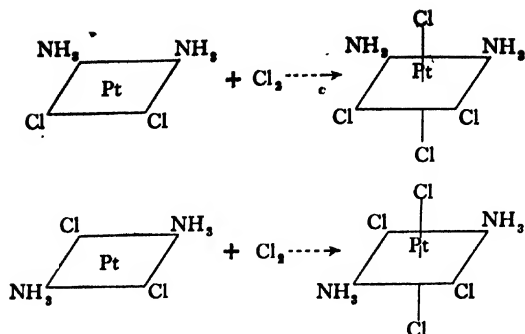


It is seen that complexes of this type with a tervalent central atom, e.g. aluminium or gold, are non-electrolytes, the central atoms in these cases being able to satisfy the three principal valencies of the acidic radicles which are found in the first sphere.

Tetrachloro Group.—A very large number of compounds are known which belong to this group. A typical platinum compound, obtained by the reduction of potassium hexachloro platinate by sulphurous acid, has the composition corresponding to the formula $\text{PtCl}_4 \cdot 2\text{KCl}$, but this mode of formulation does not agree with its reactions. Qualitative tests indicate the presence of potassium ions and a complex anion. Conductivity and molecular weight determinations indicate a ternary electrolyte. It is therefore given the co-ordination formula $[\text{PtCl}_4]\text{K}_2$, i.e. the compound is potassium tetrachloro platinite. Silver nitrate reacts with a solution of this complex salt, giving a red precipitate of the silver salt of the complex, $[\text{PtCl}_4]\text{Ag}_2$. Similar tetrahalide complex salts are formed with zinc, cadmium, mercuric mercury, and copper as central atoms.

In dealing with the methods of investigating inorganic complex salts the catalytic method was mentioned (see introduction to Chapter II). The application of the method will now be given. Bredig and Walton¹ studied the catalytic decomposition of hydrogen peroxide by the iodide ion, and found that the rate of decomposition was proportional to the concentration of this ion. The addition of a cadmium salt to a solution of potassium iodide was found to decrease its catalytic effect, i.e. to decrease the concentration of the iodide ion. This could only be explained by assuming the formation of a complex salt, which did not give iodide ions in aqueous solution. This complex salt can be obtained quite readily, and it is found to

¹ *Zeit. f. phys. Chem.*, 47, 184 (1904)



The cis-dichloro-diammine complex adds chlorine to give the quadrichloro-cis-diammine complex; the trans-dichloro-diammine, on the other hand, gives the trans product. The configuration of the product can be investigated by the methods given in Chapter III, and hence the configuration of the initial isomers can be determined. Cf. Vernon's configuration for tellurium compounds.¹

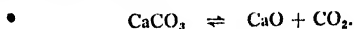
¹ *Chem. Soc. Trans.*, 117, 889 (1920).

CHAPTER IX

Stability of Inorganic Complex Salts

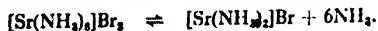
We will now consider the question of the stability of the co-ordinated complex. In some cases the complex breaks up very readily into its component parts, whereas in others it is fairly stable. We will study this question in two ways, (1) dissociation of the solid by the application of heat, (2) dissociation of the complex in aqueous solution, i.e. secondary ionization resulting from the breaking up of the complex:

The dissociation of the solid can best be studied by the application of the phase rule. We will first consider a familiar case of dissociation, that of calcium carbonate. This compound dissociates into calcium oxide and carbon dioxide:



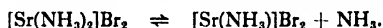
We have here a two-component system, and, therefore, in the presence of the two solid phases and the gaseous phase the system is univariant. For each temperature there is a definite pressure of carbon dioxide in equilibrium with the two solid phases, i.e. for each temperature there is a fixed dissociation pressure which is characteristic of the carbonate, and is a measure of its stability. The dissociation pressures of the carbonates of calcium, strontium, and barium can be measured at the same temperature, and will be found to decrease in the order given; this is also the order of increasing stability.

If, now, we examine the amines of any particular substance, e.g. those of strontium bromide,¹ we find the same behaviour as in the above cases. Strontium bromide forms three amines, $[\text{Sr}(\text{NH}_3)_6]\text{Br}_2$, $[\text{Sr}(\text{NH}_3)_4]\text{Br}_2$, and $[\text{Sr}(\text{NH}_3)_2]\text{Br}_2$. If the octamine is heated it dissociates into the diammine and ammonia:



¹ Hüttig, *Zeit. anorg. Chem.*, 124, 322 (1922).

In the presence of the two solid phases there is for each temperature a definite dissociation pressure. If the ammonia is removed from the system, then more of the octammine dissociates, until the pressure of the gas is equal to the dissociation pressure of the octammine at that particular temperature. Continuous removal of the gas will therefore result in the continuous dissociation of the octammine complex until it has all disappeared. The diammine will then begin to dissociate into the monammine and ammonia, and the pressure will fall to the dissociation pressure of the diammine:



Removal of the gaseous ammonia will result in a complete dis-

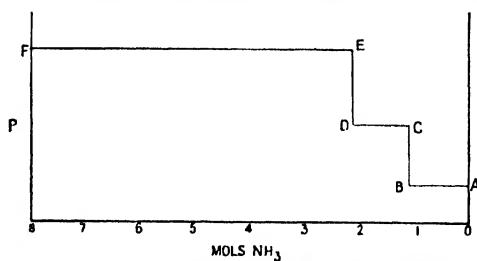


Fig. 10.—Isothermal Diagram of Amines of Strontium Bromide

sociation of the diammine into the monammine, the end of this process being indicated by another sudden drop in the pressure to a new value, which now corresponds to dissociation pressure of the monammine:



The phenomena observed when ammonia gas is brought into contact with strontium bromide at the temperature t are represented by fig. 10, in which NH_3 molecules are represented by abscissæ and pressures by ordinates. As NH_3 gas is gradually brought into the space above the salt it will be absorbed to form the monammine $\text{SrBr}_2 \cdot \text{NH}_3$, and the pressure cannot rise permanently above that indicated by the point A as long as any SrBr_2 remains uncombined. The constancy of pressure during this absorption of NH_3 , which is the pressure of ammonia in equilibrium with the solid mixture SrBr_2 — $\text{SrBr}_2 \cdot \text{NH}_3$, is represented by the horizontal line AB. When, however, all the salt has been converted into the monammine a new condition arises; for the monammine is free to combine with more

ammonia to form the diammine under increasing pressure of the gas. This pressure, however, cannot rise above the ordinate of the point C so long as any monammine remains in the solid; and it corresponds with the equilibrium between ammonia gas and a solid mixture consisting of monammine and diammine. Finally, when all the monammine has disappeared, a condition represented by the point D in the figure, the pressure rises to a value represented by the point E, whilst octammine begins to be formed. The pressure

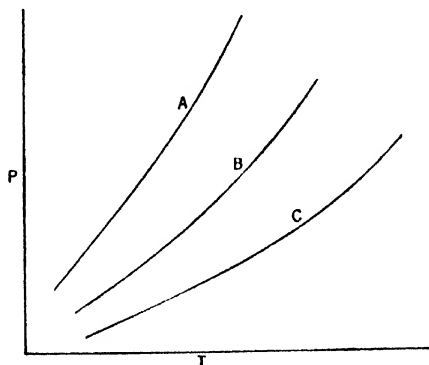


Fig. 11

represented along the line EF is that of ammonia in equilibrium with the diammine and octammine during the formation or the dissociation of the latter, and this pressure cannot be exceeded so long as any diammine remains.

As the temperature increases the dissociation pressure increases. The curves showing the relationship between the temperature and the pressure are shown for the complex amines in fig. 11. Curve A represents the dissociation pressure of the octammine at different temperatures; curves B and C show the relationship in the case of the diammine and the monammine respectively.

A method for discovering the existence of intermediate hydrates of salts, which was employed by Ramsay¹ and later by Caven and Ferguson,² consists in heating a weighed quantity of the hydrated salt in an oven to a constant temperature for certain periods of time, and then plotting loss of weight against time. The form of the

¹ *Chem. Soc. Trans.*, 32, 395 (1877). ² *Chem. Soc. Trans.*, 121, 1406 (1922).

resulting curve indicates what hydrate is stable at the temperature chosen, since the curve approaches a straight line corresponding with the loss of an integral number of molecules of water of crystallization.

Ephraim and Biltz have carried out a number of investigations of the above kind, and compared the stabilities of different complex ammines. Ephraim¹ found, for example, the temperature necessary to give a certain dissociation pressure, as follows:

Central Atom.	Atomic Volume.	Dissociation Temperature for 500 mm. Pressure.			
		Chloride.	Bromide.	Iodide.	Sulphate.
		Deg. C.	Deg. C.	Deg. C.	Deg. C.
Ni.	6.59	165	195.5	225.5	125
Co.	6.77	130	165.5	188	105.5
Fe.	7.12	106.5	141	174	96
Cu.	7.12	95	106	—	91
Mn.	7.43	79.5	121.5	164	67
Zn.	9.9	51	59.5	55.5	26
Cd.	12.9	50.5	74.5	97.5	50
Mg.	14.0	24.5	10.0	20	—

Hg, Sn, Pb, S > 14. Compounds with 6NH₃ cannot be prepared at ordinary temperatures.

Ephraim pointed out that the dissociation temperature falls with increasing atomic volume. From the above table it is also seen that the influence of the atomic volume decreases with increasing atomic volume. The empirical expression $\frac{3}{T} \cdot \frac{3}{\sqrt{V}}$ (T represents the absolute temperature and V the atomic volume of the central atom) is found to give fairly constant values, which in the above examples are: chlorides 13.8 to 14.2, bromides 13.9 to 14.5, iodides 14.4 to 14.8, sulphates 13.6 to 13.9. The atomic volume of the central atom is evidently not the only factor which determines the dissociation temperature. This is found to be greater for the iodide than for the bromide, and again higher for the bromide than for the chloride. The quotient of the absolute dissociation temperature in the case of two different halides was called by Ephraim the tension modulus. This is found to have a constant value, e.g.

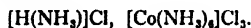
$$\frac{T(\text{NiBr}_2)}{T(\text{NiCl}_2)} = 1.073, \quad \frac{T(\text{CoBr}_2)}{T(\text{CoCl}_2)} = 1.086.$$

Ephraim further investigated salts of the same complex, i.e. where

¹ Ber., 451, 1322 (1912); 46, 3742 (1913); 47, 1928 (1914); 48, 41, 1770 (1915); 49, 529 (1916); 50, 1088 (1917); 51, 130, 706 (1918); 52, 941 (1919).

STABILITY OF COMPLEX SALTS IN SOLUTION 87

the central atom remained unchanged. Salts formed with the strong acids were found to be more stable than those with the weaker acids. The order of increasing stability is practically the same as for the ammonium salts; this supports Werner's idea that the ammonium salts should be regarded as co-ordination compounds with the hydrogen as the central atom:



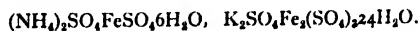
The stability of the complex amines is thus dependent on the central atom and on the anion.

Ephraim¹ also investigated the dissociation pressures of the perhalides. He found that the presence of an iodine atom rendered the perhalide almost as stable as the periodides; the stability is considerably less in those compounds which do not contain an iodine atom, whereas the absence of a bromine atom as well affects the stability to such an extent that he could not prepare perchlorides.

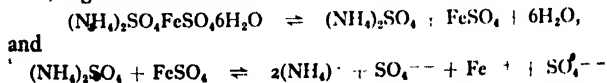
STABILITY OF COMPLEX SALTS IN SOLUTION

Mention has already been made of Hittorf's work on the transport numbers of ions; this led him to divide the double salts into two classes, (1) those which behave as mixtures of the components, (2) those which give complex ions. Ostwald called the latter complex salts, and reserved the term double salts for the former. The following examples will make this classification clear.

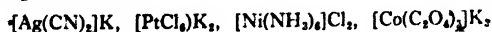
Double Salts:



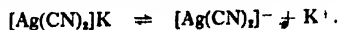
Aqueous solutions of these behave as mixtures of the component salts; e.g.



Complex Salts:



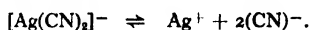
Aqueous solutions in these cases give complex ions, e.g.



There is, however, no absolute difference between these two

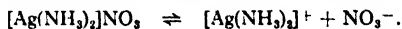
¹ *Ber.*, 50, 1069 (1917).

classes; it is merely a difference of degree of ionization. Concentrated solutions of ferrous ammonium sulphate, for example, contain complex ions, and very dilute solutions of potassium silver cyanide contain silver and cyanide ions, i.e. the complex ions undergo ionization:

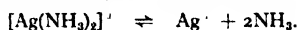


This is known as secondary ionization of the salt. Complex salts vary considerably in the degree of this secondary ionization, which is, of course, a measure of their instability. The complex cyanides of silver and iron are very stable, whereas many of the complex oxalates behave to a large extent as double salts. Two methods have been employed for measuring the stability of these complex ions, (1) precipitation method, (2) electromotive force method.

The Precipitation Method.—In discussing hexammine-cobaltic chloride, it was mentioned that a solution of the complex salt gave no precipitation with sodium hydroxide in the cold, but that the addition of ammonium sulphide produced an immediate precipitate of cobalt sulphide. The solubility product of cobalt sulphide is much less than that of the hydroxide, and, therefore, a sulphide is a more sensitive reagent for the cobalt ion than a hydroxide. In the above, ammonium sulphide indicates the presence of cobalt ions in solution, whereas their presence is not shown by the addition of sodium hydroxide. By employing reagents of different sensibility, the concentration of the metallic ion in solution can be determined. Böldander has employed this method to find the concentration of silver ions in solutions of complex silver salts. If to a solution of silver nitrate ammonium hydroxide solution is added drop by drop, a precipitate of silver hydroxide is produced; this precipitate dissolves in excess of ammonia to form the complex salt $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$. An aqueous solution of this complex ionizes as follows:



The complex ion also undergoes dissociation to a certain extent:



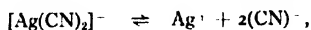
Applying the law of mass action to this latter dissociation, we get

$$\frac{[\text{NH}_3]^2 \times [\text{Ag}^+]}{[\text{Ag}(\text{NH}_3)_2^+]} = K \text{ (instability).}$$

The larger this constant is, the more unstable is the ion, hence Böldander called it the instability constant. The addition of 1 c. c.

STABILITY OF COMPLEX SALTS IN SOLUTION 89

of molar sodium bromate to 10 c. c. of 0.05 molar silver nitrate forms a heavy precipitate of silver bromate, AgBrO_3 . If, however, the bromate solution is added to the corresponding solution of diammine-silver nitrate, no precipitate results. The addition of 1 c. c. of 0.1 molar sodium chloride produces an immediate precipitate of silver chloride. Silver chloride is 2500 times as insoluble as silver bromate, the solubility products being 2×10^{-10} and 0.5×10^{-4} respectively, hence a much smaller concentration of silver ion is required to produce a precipitate of silver chloride than to produce a precipitate of the bromate. From the above equation, it is seen that the addition of ammonia reduces the dissociation of the complex ion. If sufficient excess is added, then, the concentration of silver ion is so reduced that the addition of a chloride fails to produce a precipitate. It can be found experimentally what excess of ammonia will be necessary to just prevent this precipitation, and from this and the above data, the concentration of silver ion in a solution of the complex salt can be calculated. Bödländer¹ thus found the value of the instability constant to be 6.8×10^{-8} at 25° C. In the same way he found the value of the constant in the case of potassium silver cyanide $[\text{Ag}(\text{CN})_2]\text{K}$. The complex ion produced by this salt dissociates as follows:



and therefore

$$\frac{[\text{Ag}^+][\text{CN}^-]^2}{[\text{Ag}(\text{CN})_2^-]} = K (\text{instability}).$$

The constant was found to be 1×10^{-21} ; this shows that the complex cyanide is much more stable than the ammine. Thus silver chloride cannot be precipitated by the addition of a chloride to a solution of potassium silver cyanide.

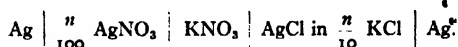
The stability of these complex ions is very important in chemical analysis, and its application will be discussed in a later chapter.

The Electromotive Force Method. If a rod of zinc be held in a solution of copper sulphate, zinc goes into solution and copper is thrown out of the solution. Zinc is therefore said to be more electropositive than copper, i.e. zinc has a greater tendency to form ions than copper. Similarly zinc will displace hydrogen from a solution of an acid, since it is more electropositive than hydrogen. Copper, on the other hand, is less electropositive than hydrogen, and will therefore not displace it from acids. The tendency with

¹ Bödländer and Fittig, *Zeit. phys. Chem.*, 39, 602 (1903).

which a metal drives its ions into solution is known as its solution pressure, and the tendency of ions to give up their charge and deposit on the metal is known as the deposition pressure. A zinc rod in contact with a solution of a zinc salt tends to send zinc ions into solution with a force proportional to its solution pressure; the zinc ions on the other hand tend to give up their charge and be deposited with a force proportional to the deposition pressure. The net result of these two tendencies will depend on the concentration of the solution. If the solution is dilute, then zinc will send some positively charged zinc ions into solution, and, consequently, the metal becomes negatively charged relative to the solution; the more dilute the solution the higher is the relative charge. If, on the other hand, the solution is very concentrated, then some of the positively charged zinc ions may be deposited on the zinc; this gives the rod a positive charge relative to the solution. We thus see that the charge of a metal relative to the solution, i.e. the electrode potential of the metal, depends on the concentration of the solution. Since the electrode potential of a metal in contact with a solution of its salt depends on the concentration of the metallic ions, measurement of the former can be used to determine the latter. The electromotive force of a cell is due to the differences of potential at its electrodes; if, therefore, we have two electrodes of the same metal immersed in solutions of a salt of the metal of different concentrations, the two electrodes will be at different potentials and on being connected a current of electricity will be obtained. Such an arrangement is known as a concentration cell, and its electromotive force is due to the different concentrations of the two solutions. By concentration is understood the concentration of the metallic ions.

The above gives us a method of finding the concentration of ions of a metal in a solution, and has been largely employed for finding the solubility of sparingly soluble salts. Thus the solubility of silver chloride can be found by finding the e.m.f. of the following cell:



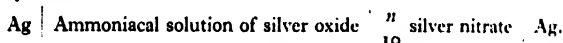
This enables us to find the concentration of silver ions in the KCl solution; the concentration of chloride ions is known, hence the solubility product of the silver salt can be found. The concentration of the silver is found from the e.m.f. by means of the expression

$$\text{e.m.f.} = \frac{v}{u+v} \frac{2 \times 0.058}{n} \log_{10} \frac{C_1}{C_2}$$

STABILITY OF COMPLEX SALTS IN SOLUTION 91

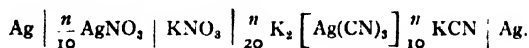
In this equation $\frac{v}{u+v}$ is the transport number of the anion, n is the valency of the metal ion, C_1 and C_2 are the ionic concentrations of the metallic ions in the two solutions.

This method has been employed with success by Bödlander to find the concentration of silver ions in solutions of complex silver salts. Thus in the case of diammine-silver nitrate, a measurement of the e.m.f. of the following cell enables one to find the degree of dissociation of the complex ion.



The instability constant of the complex ion can thus be found. The results obtained by this method agree very well with those obtained by the solubility method.

Similarly the stability of the complex $[\text{Ag}(\text{CN})_3]^{--}$ can be found from the e.m.f. of the cell.



$$K (\text{instability}) = \frac{[\text{Ag}^+][\text{CN}^-]^3}{[\text{Ag}(\text{CN})_3]^{--}}.$$

These instability constants have been investigated more especially from the point of view of chemical analysis, and have proved of very great value in that branch of chemistry; they enable us to calculate the sensitiveness of various tests and the completeness of different separations. This important application will be discussed in the next chapter.

It has already been pointed out that there is no absolute difference between complex salts and double salts. Potassium ferricyanide might be regarded as a typical complex salt because of the stability of the ion $[\text{Fe}(\text{CN})_6]^{--}$, whereas ferrous ammonium sulphate gives rise to a very unstable complex ion $[\text{Fe}(\text{SO}_4)_2]^{--}$, and is consequently regarded as a typical double salt. A large number of salts give rise to complex ions, whose stabilities vary from that given by potassium ferricyanide to that given by ferrous ammonium sulphate, and it is often difficult to know whether to classify them as complex or double salts.

Sufficient data are not available to compare the stabilities of these complexes in solution with the atomic volumes of the central atoms, and to find whether the stabilities are in the same order as that found by the phase rule method.



CHAPTER X

Inorganic Complex Salts and Chemical Analysis

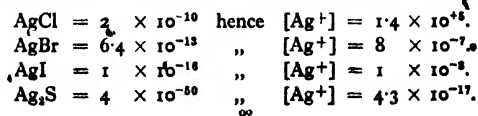
We will now consider the application of inorganic complex salts in chemical analysis. It will be seen that, in practically all cases, this application is based on the differences in the stability of their complex ions. The different separations will be discussed briefly, and their principle explained.

APPLICATION TO QUALITATIVE ANALYSIS

Chlorides, Bromides, and Iodides.—The silver salts of these three acidic radicles are very sparingly soluble in water, the chloride and bromide are soluble in ammonia, whereas the iodide is practically insoluble. The instability constant of the complex diammine-silver ion $[\text{Ag}(\text{NH}_3)_2]^+$ was found by Bödlander to be 0.5×10^{-3} . It has already been seen that a solution of this complex gives a precipitate with a solution of a chloride. The dissociation of the complex ion can be reduced by the addition of excess of ammonia, in accordance with the law of mass action:

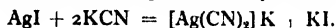


If sufficient excess of ammonia is added, then the precipitation of the chloride and even the bromide of silver does not take place on the addition of the usual reagents; silver iodide is, however, so insoluble, that excess of ammonia cannot prevent its precipitation. This shows the sensibility of the iodide test for silver ion. The solubility products of some of the sparingly soluble silver salts are:

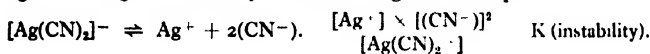


The iodide can thus be separated from the chloride and bromide by means of a solution of ammonia. The chloride and bromide can be further separated by fractional dissolution in ammonia; the ammonia being gradually added, the more soluble chloride being first dissolved.

The diammine-silver complex is, as we have seen, too unstable to prevent the precipitation of silver iodide, or, what amounts to the same thing, ammonia will not dissolve silver iodide. Silver iodide is, however, readily soluble in potassium cyanide solution:



This complex salt ionizes to give the complex ion $\text{Ag}(\text{CN})_2^-$, and this again undergoes secondary ionization to give the simple ions.



The fact that an iodide does not precipitate silver iodide from a solution of this complex points to the great stability of the latter. Bödlander found the instability constant (by the methods already discussed in a previous chapter) to be 1×10^{-22} . Silver iodide also dissolves in a solution of sodium thiosulphate to form the complex salt $[\text{AgS}_2\text{O}_3]\text{Na}$, hence the complex ion $[\text{AgS}_2\text{O}_3]$ must be very stable. The addition of a sulphide to a solution of any of these complex salts of silver produces an immediate precipitate of silver sulphide. This shows the extreme insolubility of silver sulphide.

The solubility of silver chloride in ammonia is employed for the separation of silver and mercurous mercury in the first group of qualitative analysis, mercurous chloride turning black in the presence of ammonia, owing to the formation of a black mixture of $\text{Hg} + \text{HgNH}_2\text{Cl}$.

Copper and Cadmium.—The separation of copper and cadmium is based on the difference in stability of their complex cyanides. After the elimination of the other members of group 2, ammonia is added gradually to the solution of the nitrates of these two metals until the precipitated hydroxides first formed redissolve, forming complex amines, $[\text{Cu}(\text{NH}_3)_4]\text{X}_2$ and $[\text{Cd}(\text{NH}_3)_4]\text{X}_2$.¹ The former of these is dark blue and so the presence of copper is readily detected. A solution of potassium cyanide is then added until the blue colour disappears, and H_2S gas bubbles through, when cadmium sulphide only is precipitated, despite the fact that copper sulphide is the more insoluble

¹ Locke and Forsall, *J. A. C. S.*, 31, 268, 297 (1904); Dawson, *Chem. Soc. Trans.*, 89, 1674 (1906).

of the two sulphides, its solubility product being 8.5×10^{-46} as compared with 3.6×10^{-29} for cadmium sulphide. The addition of potassium cyanide solution to the complex amines causes the formation of complex cyanides, potassium cuprocyanide, $[\text{Cu}(\text{CN})_4]\text{K}_2$, and potassium cadmium cyanide, $[\text{Cd}(\text{CN})_4]\text{K}_2$. The instability constants¹ of these complex salts are 0.5×10^{-27} and 1.4×10^{-17} respectively, and the greater stability of the copper compound more than counteracts the greater insolubility of the copper sulphide.

Cobalt and Nickel.—Two of the methods employed for the separation of cobalt and nickel have as their basis the different stabilities of complex ions containing these metals.

(a) *The cyanide method.* Cobalt and nickel form complex cyanides having the formulæ $[\text{Co}(\text{CN})_6]\text{K}_3$ and $[\text{Ni}(\text{CN})_4]\text{K}_2$, the former being the more stable. Bromine and alkali have no effect on the cobalt complex, whereas, in the case of the nickel complex, an immediate precipitate of hydrated nickel dioxide appears.

(b) *The carbonate method.* If to a mixture of cobalt and nickel salts is added a large excess of sodium bicarbonate and bromine water, and the mixture gently warmed, the presence of cobalt is indicated by the formation of a dark green solution, whereas nickel produces a precipitate of a higher oxide of nickel, generally deposited as a mirror on the sides of the tube. The dark green solution contains the complex salt sodium cobalti-carbonate, $[\text{Co}(\text{CO}_3)_3]\text{Na}_3$, but the complex carbonate of nickel is not sufficiently stable to exist in the presence of alkali and bromine. The dimethylglyoxime test for nickel will be considered later.

A very complete separation of nickel from cobalt may be effected by reducing to the metallic state and removing the nickel in the form of volatile nickel carbonyl, $[\text{Ni}(\text{CO})_4]$, by heating in a current of carbon monoxide. Cobalt does not form a carbonyl under the same conditions.

Potassium is recognized by the formation of sparingly soluble complex salts, $[\text{PtCl}_6]\text{K}_2$, potassium platinichloride, and $[\text{Co}(\text{NO}_2)_4]\text{K}_2$, potassium cobaltinitrite. The corresponding sodium salts are readily soluble in water; the ammonium salts are, however, but sparingly soluble and must not be mistaken for the potassium salts.

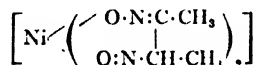
Complex salts have also proved of value in the separation of the less common elements. Thus caesium can be separated from rubidium by the addition of stannic chloride in the presence of strong hydrochloric acid, caesium hexachloro-stannate, $[\text{SnCl}_6]\text{Cs}_3$, being less

soluble than the corresponding rubidium salt. Iridium can be separated from platinum by the addition of potassium nitrate to a solution of the chlorides, under which conditions iridium forms a sparingly soluble double complex salt $\frac{1}{3}[\text{Ir}(\text{NO}_2)_6]\text{K}_3 \cdot [\text{Ir}(\text{Cl})_6]\text{K}_3$, tripotassium hexanitro iridate potassium hexachloro iridate, the platinum remaining in solution. Quadrivalent palladium gives the same reactions as the bivalent ion, owing to the readiness with which the former is reduced to the latter. The two ions can, however, be distinguished by the fact that with potassium chloride the quadrivalent ion gives a red crystalline precipitate of the complex salt $[\text{PdCl}_6]\text{K}_2$.

APPLICATION TO QUANTITATIVE ANALYSIS

Co-ordination compounds have also found an important application in quantitative analysis, the inner complex salts figuring very largely in this field.¹ Some of these applications will be discussed very briefly.

Tschugaeff² found that a beautiful red, highly insoluble inner complex salt is formed when an alcoholic solution of dimethylglyoxime is added to an ammoniacal solution or acetic acid solution of a nickel salt.



This compound contains 20.33 per cent of the metal and may be weighed as such, or ignited to the oxide. Tschugaeff claims that by means of dimethylglyoxime as a reagent, the presence of one part of nickel can be detected in the presence of 5000 parts of cobalt. α -benzildioxime is a still more sensitive reagent for nickel; it gives a red precipitate with a salt of this metal which is insoluble in water, alcohol, acetone, ammonia, and dilute acetic acid. By means of this dioxime one part of nickel in 5,000,000 parts of water can be detected. The inner complex salt formed contains 10.93 per cent nickel, $\text{C}_{28}\text{H}_{22}\text{N}_4\text{O}_4\text{Ni}$.

The above methods can be employed for the estimation of nickel in the presence of cobalt, manganese, zinc, chromium, and iron.

Baudisch³ has shown that nitrosophenyl-hydroxylamine (cupferron) can be employed for the separation of iron and copper

¹ Lowry, *J. S. C. I.*, **42**, 462 (1923). ² *Ber.*, **38**, 2520 (1905).

³ *Chem. Zeit.*, **33**, 1298 (1909).

from all the other metals, this being due to the formation of sparingly soluble complex salts.

Cobalt forms a purple-red complex salt with β -naphthaquinone, which when precipitated in acetic acid solution can be employed for the quantitative estimation of cobalt in the presence of nickel.

Potassium can be estimated by weighing the sparingly soluble platinichloride, $[\text{PtCl}_6]\text{K}_2$, or the cobaltinitrite, $[\text{Co}(\text{NO}_2)_6]\text{K}_3$.

Complex salts have also found application in volumetric analysis. When boric acid is titrated against sodium hydroxide, using phenolphthalein as indicator, a faint red colour is formed before all the boric acid has been neutralized to form the metaborate. Jørgensen¹ found that the addition of glycerine or mannitol to the boric acid gave a very sharp and accurate end point. The action of the glycerine or mannitol is due to the formation of a strong complex acid, $[\text{C}_3\text{H}_5\text{O}_2(\text{OH})\text{BO}]\text{H}$, whose sodium salt is not hydrolysed.

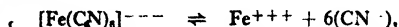
An iodometric method for the estimation of ferric iron can be employed if sodium pyrophosphate is added to the solution. Romijn² found that ferric iron forms a very stable complex salt with the phosphates, $[\text{Fe}(\text{PO}_4)_2]\text{M}_3$, so that ferric ions can be removed from solution by the addition of a phosphate, and therefore the reversible reaction



is rendered irreversible.

Dede³ found that copper also forms a complex phosphate, which, however, is decomposed in the presence of acids; the ferri-complex is stable in the presence of acids. Hence the copper in a mixture of cupric and ferric salts can be estimated by titration with iodine in the presence of a phosphate and free acid.

The Analysis of a Complex Salt.—The analysis of a complex salt sometimes offers great difficulties. This occurs when the complex ion is so stable that the reactions of the components of the co-ordinated complex are not given, as has already been shown to be the case with the complex cuprocyanide and the complex cobaltcyanide. Potassium ferricyanide, $[\text{Fe}(\text{CN})_6]\text{K}_3$, may be cited as a further example. The ferricyanide complex ion is very stable, the concentration of ferric ion being so low that it is not detected even by the delicate thiocyanate test. On examining the dissociation of the complex ion,



¹ *Zeit. angew. Chem.*, 5, 6 (1897).

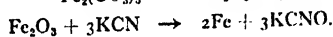
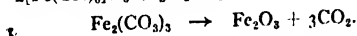
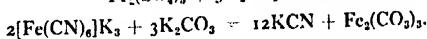
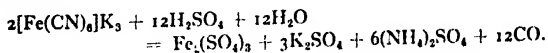
² *Chem. Zeit.*, 35, 1300 (1911).

³ *Zeit. anorg. Chem.*, 125, 45 (1922).

it is seen that the removal of the cyanide ion would increase the decomposition of the complex. The addition of mineral acid to the solution would introduce hydrogen ions, and since hydrocyanic acid is a very weak acid, this would remove the cyanide ions, and consequently increase the concentration of the ferric ion.

If ether is shaken with a solution of potassium ferricyanide and a thiocyanate, no trace of colour is shown; if, however, concentrated hydrochloric acid is added to the solution, the ether becomes distinctly pink. Sherril¹ found that the dissociation constant for mercuric cyanide is extremely small, being far less than that for hydrocyanic acid. A mercuric salt thus acts more effectively than an acid in suppressing the cyanide ion, and can be used in place of the hydrochloric acid in the above experiment with ether and a thiocyanate.

The components of the co-ordinated complex can also be detected by destroying the complex. This is generally carried out by evaporating with concentrated sulphuric acid or by fusion with alkali carbonate. In the case of the ferricyanide the following reactions take place:



In some cases, gently warming the solution is sufficient to give the ionic reactions; e.g. a solution of potassium cobalti-oxalate, $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{K}_3$, gives the reactions of the cobalt and the oxalate ion if the solution is warmed. In other cases the complex ion is sufficiently unstable to give all the reactions in the cold, e.g. potassium ferri-oxalate, $[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{K}_3$.

• • The ferri- and ferro-cyanides are employed to distinguish between ferric and ferrous salts. A ferric salt gives with a solution of potassium ferrocyanide a dark blue precipitate of ferric ferrocyanide, $[\text{Fe}(\text{CN})_6]\text{Fe}_3$ (Prussian blue), a white precipitate being given by a ferrous salt. A solution of ferrous salt gives with a solution of potassium ferricyanide a dark blue precipitate of ferrous ferricyanide, $[\text{Fe}(\text{CN})_6]\text{Fe}_2$ (Turnbull's blue), a ferric salt under the same conditions producing a brown coloration. This also explains the use

¹ *Zeit. phys. Chem.*, 43, 705 (1903).

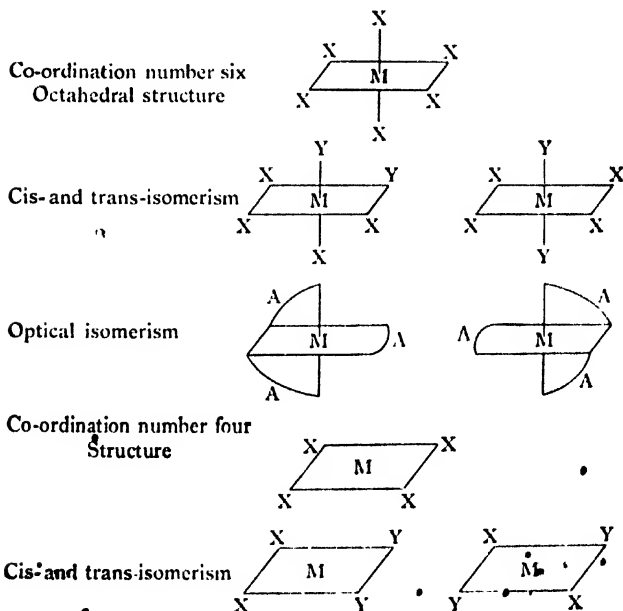
of a ferricyanide as an outside indicator in the titration of ferrous salts with dichromate. The production of a blue colour indicates the presence of a ferrous salt and therefore the incompleteness of the oxidation.

The quantitative analysis of a complex salt requires the same precautions as were taken in its qualitative analysis. To estimate the components of a complex ion, the latter must be destroyed as described under qualitative analysis. An example is given in Chapter XII.

CHAPTER XI

Résumé

In the preceding chapters the complex salts with co-ordination numbers of six and four have been discussed. They are here summarized:



It is proposed now to review very briefly these compounds and to refer to other types having a different co-ordination value.

Co-ordination Number Six.—Most of the complex salts

belong to this group. In these compounds the six co-ordinated groups are symmetrically arranged around the central atom, being situated at the corners of a regular octahedron surrounding the attracting atom as centre. This structure is in accordance with the number and types of isomers exhibited by these compounds. The isomerism most frequently met with depends upon the *cis* and *trans* structure; the configuration is found by methods analogous to those employed in organic chemistry. Certain salts of this series exhibit optical isomerism, this being in accordance with the octahedral structure which gives compounds, e.g. of the type $[M(en)_3]$, an asymmetric configuration. The existence of compounds of this type in the optically active state demonstrates very clearly that the one and only condition of optical activity is molecular asymmetry, the identity or otherwise of the groups surrounding the central polyvalent atom being of no importance.

The study of these compounds implies:

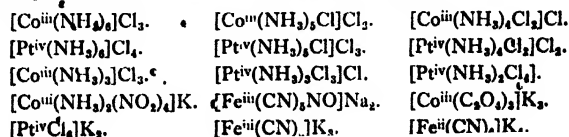
(1) Determination of the number of ions given by each molecule in a dilute aqueous solution. This can be carried out in two ways: (a) by molecular weight determination, and (b) by determination of molecular conductivity at different dilutions.

(2) Determination of the nature of the ions present. This can be carried out by (a) the application of qualitative tests, and by (b) the electromotive force method. These investigations are fully discussed in Chapters II and IX.

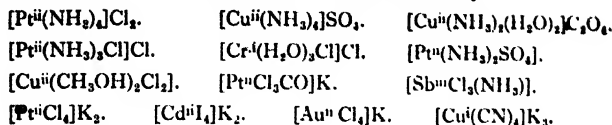
Co-ordination Number Four.—In these complexes four groups or atoms are co-ordinated around the central atom. The number and types of isomers indicate that these four groups all lie in the same plane as the central atom and are symmetrically arranged around it. The methods of study are analogous to those employed for the compounds with co-ordination number equal to six.

Valency.—In all these compounds, the valency of the complex is equal to the valency of the central atom minus the number of univalent negative groups or their equivalent in the co-ordinated complex. For example:

Complex salts with co-ordination number equal to six—



Complex salts with co-ordination number equal to four—

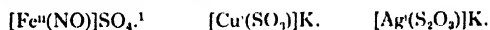


It is thus seen that one and the same central atom may give complex salts producing complex anions or complex cations, or even a non-electrolyte. The nature of the complex ion produced depends on the valency of the central atom and on the nature of the co-ordinated groups.

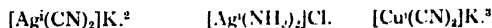
The isomerism and structure of the complexes is shown on p. 99.

A number of complex salts are known with co-ordination number other than six or four. Many of these are of considerable importance in chemical analysis (see Chapter X) and their relative stabilities have been investigated, but very little work has been done on their configuration. The following may serve as examples of these different types of compounds:

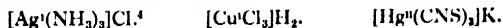
Co-ordination number—one:



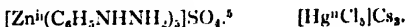
Co-ordination number—two:



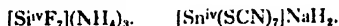
Co-ordination number—three:



Co-ordination number—five:



Co-ordination number—seven:



Co-ordination number—eight:



It is seen from this list that the same central atom may form

¹ Marchot, *Ber.*, **47**, 1601 (1914). ² Euler, *Ber.*, **36**, 1859² (1903).

³ *Ibid.*, 1854.

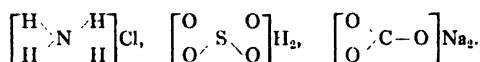
⁴ Gmülin Kraut, Vol. II, 1459.

⁵ Grossmann and Hünseler, *Zeit. anorg. Chem.*, **46**, 403 (1905).

⁶ Hüttig, *Zeit. anorg. Chem.*, **124**, 322 (1922).

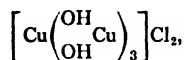
complex salts with various co-ordination numbers; in such cases the most stable is generally the salt exhibiting the maximum co-ordination number of the metal. The more common complexes are those with co-ordination numbers two, four, six, and eight, these numbers of groups lending themselves more readily to a symmetrical arrangement of the groups around the central atom.

The co-ordination theory has been applied by Werner to the ammonium salts, the sulphate and carbonate radicles, &c., i.e. to compounds which are generally represented by the ordinary valencies. Formulated according to the co-ordination theory, these compounds are represented thus:



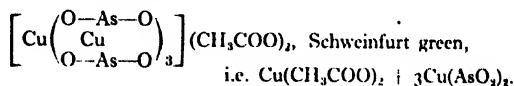
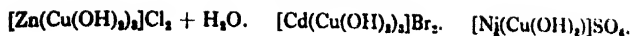
Similarly Werner represents all the carbon compounds as co-ordination compounds with carbon as the central atom, these compounds showing a co-ordination number of four. It may be pointed out that in the complex salts the four groups are in the same plane as the central atom, whereas in the carbon compounds they are arranged at the corners of a regular tetrahedron with the carbon atom at the centre.

Basic Salts. - Werner¹ applied the co-ordination theory to explain the structure of basic salts. If we consider a hexa-aquo compound, the co-ordination points are here occupied by six molecules of water, i.e. by six molecules of hydrogen hydroxide; Werner now claims that these six molecules are replaceable by six molecules of a metallic hydroxide yielding a basic salt. Take, for example the compound $[\text{Cu}(\text{H}_2\text{O})_6]\text{Cl}_2$; the replacement of the water molecules by their equivalent of cupric hydroxide molecules would yield the compound



i.e. basic copper chloride (cf. the replacement of six ammonia molecules by their equivalent of ethylenediamine molecules). According to this the existence of mixed basic salts is readily understood; the following are a few basic salts formulated in this way:

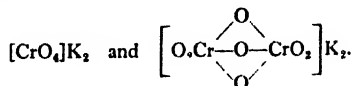
¹ *Ber.*, 40, 4441 (1907).



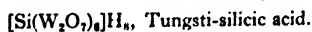
This copper salt illustrates the replacement of the co-ordinated* groups by the salt of an oxy-acid.

Poly-acids.—Miolati¹ has extended the application of Werner's theory to explain the structure of the poly-acids. Potassium chromate can, for example, be regarded as a co-ordination compound with chromium as the central atom, K_2CrO_4 , $[\text{CrO}_4]\text{K}_2$. In this complex one can imagine the replacement of an oxygen atom by the chromate radicle; this would yield the compound $\left[\text{Cr} \begin{pmatrix} \text{CrO}_4 \\ \text{O}_3 \end{pmatrix} \right] \text{K}_2$, i.e. $\text{K}_2\text{Cr}_2\text{O}_7$, a dichromate. Similarly another oxygen atom may be replaced by another chromate radicle to produce a trichromate, $\left[\text{Cr} \begin{pmatrix} \text{CrO}_4 \\ \text{O}_2 \end{pmatrix} \right] \text{K}_2$, &c. According to this formulation the dichromate would be potassium monochromato-trioxo-chromate. In the same way Miolati formulates pyrosulphates and the thio-acids as co-ordination compounds derived from sulphuric acid; thus, $[\text{SO}_4]\text{K}_2$, $\left[\text{S} \begin{pmatrix} \text{SO}_4 \\ \text{O}_3 \end{pmatrix} \right] \text{K}_2$, $\left[\text{S} \begin{pmatrix} \text{S} \\ \text{O}_3 \end{pmatrix} \right] \text{K}_2$, &c.

Werner, however, prefers to regard these poly-acids as polynuclear compounds. According to him, potassium chromate and potassium dichromate receive the formulation



In the same way the heteropoly-acids have been formulated on the basis of the co-ordination theory. Thus: $\left[\text{Cr} \begin{pmatrix} \text{SO}_4 \\ \text{O}_3 \end{pmatrix} \right] \text{M}_2$.

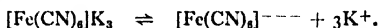


¹ *Journ. f. prakt. Chem.*, 77, 444 (1908).

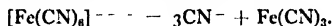
Attempts have also been made to apply the theory to the structure of the complex silicates, but without much success.

Water of Crystallization.—According to the co-ordination theory, the water of crystallization of a salt is generally regarded as forming a part of the complex, i.e. the molecules of water are regarded as being in the first sphere of influence of the metal and are therefore firmly held in the molecule, e.g. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$. It sometimes happens, however, that all the water molecules are not firmly held, and that their expulsion from the molecule does not have any appreciable effect on the character of the compound (see Chapter III), e.g. $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 + \text{H}_2\text{O}$. In this case it is assumed that the loosely held molecule is in the third sphere of influence of the metallic atom, while the co-ordinated groups are in the immediate surroundings of the metal and very firmly held; the two chlorine atoms are in the second sphere and are more loosely held—they split off as ions in solution; the last molecule of water in this particular example is then assumed to be still farther away, i.e. in the third sphere. The method of investigating such compounds has been given in Chapter III.

Factors affecting the Stability of Complex Salts.—Abegg and Bödlander¹ have shown very clearly that the stability of the complex salts depends to a large extent on the electro-affinity of the components. Electro-affinity is defined as the tendency to ion formation. A complex salt on dissolution in water undergoes ionization; one of the ionic products is a molecular compound and is made up of an ion (the ionic component) and a neutral molecule (the neutral component); for example, potassium ferricyanide ionizes in aqueous solution thus:



The ionic product $[\text{Fe}(\text{CN})_6]$ consists of the cyanide ion 3CN^- and the neutral molecule ferric cyanide $\text{Fe}(\text{CN})_3$,



The stability of this complex ion depends on the tendency of its components to ionize. We will deal briefly with the two components of the complex ion, and will try and show how each affects its formation and stability.

The Neutral Component.—It can easily be shown that the greater the tendency of the neutral component itself to dissociate

¹ *Zeit. anorg. Chem.*, 20, 471 (1899).

into ions the greater will be the instability of the complex. Hence the most suitable salts to form the neutral portion of a complex ion are those which themselves form very weak ions. Take, for example, the alkali metals; these form very stable ions in solution and would not therefore be expected to function as the components of a complex ion, which is in accordance with experience. The compounds $\text{KNa}_3(\text{SO}_4)_2$ and KNaCO_3 dissociate completely into their components when dissolved in water; in concentrated solutions, however, one would expect to find some complex ions, which are very unstable and on dilution would break up into their component ions. The existence of complex ions can even be demonstrated in concentrated solutions of a single salt, e.g. KCl in concentrated solution contains the complex ion KCl_2^- (i.e. $\text{Cl}^- + \text{KCl}$). As the positiveness of the metal decreases, the existence of the complex ions is much more readily shown; thus a concentrated solution of cadmium iodide contains the ions $[\text{CdI}_4]^{2-}$ ($2\text{I}^- + \text{CdI}_2$). The alkaline earth metals form fairly stable ions, and are not often found in complex ions. The tendency to complex ion formation is, however, much greater in the second group than in the case of the alkali metals, c.f. carnallite $[\text{MgCl}_2]\text{K}$. As we pass along to the trivalent metals, e.g. aluminium, we find that tendency has further increased; for example, cryolite, $[\text{AlF}_6]\text{Na}_3$, the alkali aluminium silicates, and especially the alums. Again, trivalent chromium is often found as the component of a complex ion; a freshly prepared solution of $[\text{Cr}(\text{SO}_4)_4]\text{H}_2$ gives no precipitate with barium sulphate. As we thus treat the metals in order of decreasing electro-affinity, we find that their tendency to form the part of a complex ion increases, and when we come finally to gold and platinum, we find metals which are hardly ever found as simple ions but almost always as parts of complex ions.

It might be interesting to consider for a moment the acid salt MHA . Will this ionize to form the ions $\text{M}^+ + \text{HA}^-$ or $\text{H}^+ + \text{MA}^-$? I.e. will the metal M or the hydrogen form the part of the complex ion? This is decided by the relative electro-affinities of the metal M and hydrogen; the less electropositive will remain as a part of the complex. This is clearly seen in the following examples: $[\text{HSO}_4]\text{K}$; $[\text{HF}_2]\text{K}$; $[\text{HCO}_3]\text{Ca}$; $[\text{HgCl}_4]\text{H}_2$; $[\text{Fe}(\text{CN})_6]\text{H}_3$; $[\text{AgBr}_2]\text{H}$; $[\text{AuCl}_4]\text{H}$; $[\text{PtCl}_6]\text{H}_2$. Similarly in the case of the salts of the type $\text{M}'\text{M}''\text{A}$, the metal with the complex ion will be the less electropositive; cf. $[\text{NaSO}_4]\text{K}$; $[\text{Cu}(\text{CN})_4]\text{K}$; $[\text{Al}(\text{SO}_4)_2]\text{K}$; $[\text{Fe}(\text{CN})_6]\text{Na}_3$; &c

The Ionic Component.—The product of electrolysis of complex salts is hardly ever the complex ion, but the component single ion, hence the electro-affinity of the complex ion is greater than that of the component ion; i.e. the electro-affinity of the ion is increased by the co-ordination of the neutral part. A complex ion breaks up spontaneously into its component parts, hence its free energy is greater than that of its components. By co-ordination with a neutral part, the volume and area of the ion are increased, but always the same charge, i.e. 96,540 Coulombs is carried for each unit of valency, therefore the potential of the ion is lowered and consequently its stability increased by co-ordination. If we consider atoms which exhibit various valencies, the higher the valency the less the electro-affinity, and, according to the above, the greater the tendency to complex ion formation. Reference has already been made to the greater stability of the ferri-, cobalti-, and chromi-complexes compared with those of the bivalent metals.

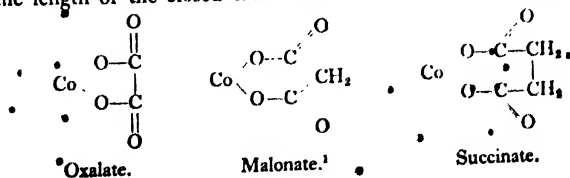
The ionic component of a stable complex ion is necessarily itself an unstable ion. Consider the anions; the nitrates, sulphates, and halides are barely ever found as components of stable complex ions. In the series chloride, bromide, iodide, cyanide, the increasing tendency to complex formation is readily seen to be associated with decreasing electro-affinity thus: KCl dissolves very little AgCl, KBr dissolves more AgBr, KI dissolves an appreciable amount of AgI, KCN dissolves an equivalent amount of AgCN. This influence is also seen in considering the relative stabilities of the following ferri-complexes: $[\text{Fe}(\text{SO}_4)_2]\text{K}$ very unstable, in dilute solution almost complete dissociation into its components; $[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{K}_3$ much more stable, but in dilute solutions partially dissociated; $[\text{Fe}(\text{CN})_6]\text{K}_3$, this is a very stable complex, and does not give the delicate thiocyanate test for the ferric ion even in very dilute solution.

In the above we have considered complex salts in which the complex ion contains a salt as the neutral component; in many cases, however, the neutral part is a simple molecule, e.g. NH_3 , and these types will be briefly discussed. From the above, the less the electro-affinity of the metal the more readily will it, for example, form complex amines. This is borne out by the examples given all through this book; the stable amines contain as central metals those which are feebly electropositive. It is also well illustrated by considering metals exhibiting various valencies; the higher valent, i.e. the less electropositive, forms the more stable complexes. The

univalent cuprous ion does not form as stable complex amines as the bivalent cupric ion. Again, the amines of bivalent cobalt and univalent mercury lose their ammonia readily at ordinary temperatures, whereas the complexes of trivalent cobalt and bivalent mercury are stable.

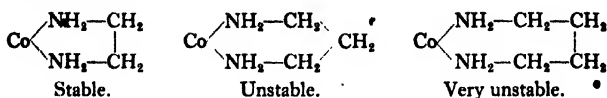
An ion will readily add on neutral molecules, if it thereby increases in strength. The soluble chromates are alkaline in reaction due to the low electro-affinity of the chromate ion; this weak ion readily co-ordinates the neutral molecule chromium trioxide to form the much more stable dichromate ion; $[\text{CrO}_4]^{--} \rightarrow [\text{CrO}_4\text{CrO}_3]$. Similarly the sulphate ion adds on sulphur trioxide to form the stronger pyrosulphate ion, $[\text{SO}_4]^{--} \rightarrow [\text{SO}_4\text{SO}_3]^{--}$, or again, sulphur dioxide to form the dithionate ion, $[\text{SO}_4]^{--} \rightarrow [\text{SO}_4\text{SO}_2]^{--}$. The greater stability of these ions is seen in the greater solubility of the barium salts. The weak silicate ion readily co-ordinates a neutral molecule such as silica, tungsten trioxide, or boron trioxide to form strong ions with non-hydrolysable salts. The employment of mannitol or glycerine in the titration of boric acid is due to the fact that the acid is considerably strengthened by the co-ordination of these hydroxy compounds. The sulphate ion can be regarded as oxygen molecules co-ordinated by the feeble sulphide ion; the association of sulphur with these ions yields the polysulphides K_2S_2 , K_2S_3 , K_2S_4 , K_2S_5 . Polyhalides can also be formed, KBr_3 , KI_3 , but these are much more unstable due to the high electro-affinity of the halide ion.

Another factor which affects the stability of complex ions in cases where groups occupy two co-ordinated points is the length of the closed chain. Take, for example, the complex salts formed by the co-ordination of the organic dibasic acids with cobalt as the central atom. The oxalate is readily prepared and is comparatively stable, the malonate is difficult to prepare and is very unstable, whereas the succinate has not been prepared. The influence of the length of the closed chain is seen from the following figures.



¹ Thomas, *Chem. Soc. Trans.*, 119, 1140 (1921).

The same results are obtained if one considers the co-ordination of the diamines:

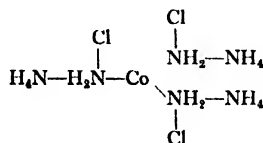


It is thus seen that the most stable complexes are those which contain five-membered rings (cf. the stabilities of the polymethylenes).

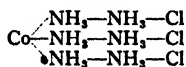
As has been discussed in a previous chapter, the relative stabilities of the complex salts are of very great importance in qualitative analysis. The knowledge of these stabilities enables one to calculate the delicacy of various tests and the completeness of separations in which complex salts are employed.

Earlier Views on the Constitution of the Complex Salts.

—The complex salts have been studied in this book from the point of view of Werner's co-ordination theory, which is the generally accepted theory of their structure. Brief mention may now be made of the earlier views on these compounds. The first ammine was discovered by Tassaert in 1794; it was described as a compound of ammonia and a cobalt salt. The first attempt to formulate these complexes was made by Hofmann in 1854, who considered them as derivatives of ammonium salts, e.g. hexammine-cobaltic chloride was given the structure:

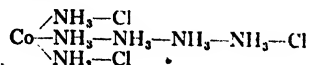


This formula does not explain the fact that on the expulsion of one molecule of ammonia, one of the chlorine atoms ceases to split off as an ion. The preparation of analogous compounds with tertiary bases (e.g. pyridine) instead of ammonia showed that the above structure was incorrect. In 1869, Blomstrand¹ published his views on these compounds; he considered that they contained chains of quinquivalent nitrogen, and hexammine-cobaltic chloride was formulated thus:

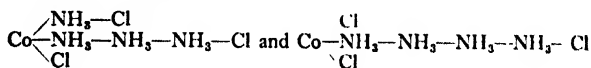


¹ *Chemie der Jetztzeit* (Heidelberg 1869)

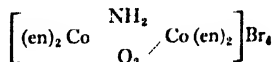
in which the three chlorine atoms were attached to quinquevalent nitrogen atoms as in an ammonium salt; this readily explains their ionic character, but does not explain the influence of the driving of an ammonia molecule.* Jørgensen¹ modified this formula and suggested the following:



On losing one or two molecules of ammonia, one or two atoms of chlorine became directly attached to the cobalt atom, giving the following compounds:



Whilst this might explain the non-ionizable character of these two chlorine atoms, it does not explain the fact that with the loss of another molecule of ammonia a non-electrolyte is produced. It is also very difficult to explain the isomerism met with in these compounds on the assumption of these formulæ of Jørgensen. All these points are rendered clear by Werner's centric formulation, and this theory has received very strong support by the discovery of optical isomerism. It was mentioned in the earlier part of the book that Werner assumed the existence of two kinds of valencies, which he called principal and auxiliary or primary and secondary valencies; he later came to the conclusion that these two valencies were identical. He was led to this conclusion by an examination of the optical isomerism of the poly-nuclear compound



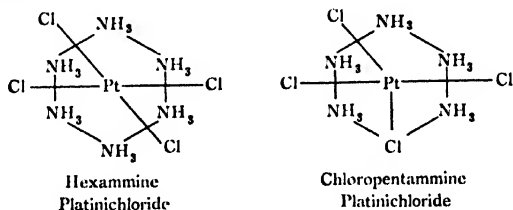
Assuming a difference between principal and auxiliary valencies, the complex would have the above structure, i.e. the two halves of the molecule are not identical, and one would expect to find two racemic compounds and four active isomers, but only one racemate and only two active isomers have been prepared, pointing to the identity of these two kinds of valency.

X-ray examination of crystals of complex salts has shown that the co-ordinated groups are arranged at the corners of a regular

¹ *Zeit. anorg. Chem.*, 24, 158 (1900).

octahedron surrounding the central atom. Thus Werner gave up his original theory of principal and auxiliary valencies, and regarded the complex as a grouping of the co-ordinated radicles around the central atom.

Friend¹ regarded the co-ordinated groups as being joined together and not to the central metal, as is seen in the following examples:



This readily explains why one chlorine atom in the second salt does not undergo ionization.

Recent theories of Lowry² and Sidgwick³ are based on the modern conception of the atom. Co-ordination of groups completes the outer sphere of electrons of the central atom by sharing the electrons of these groups, and brings about union by covalency.

¹ *Chem. Soc. Trans.*, **93**, 1006 (1908). ² *Chem. Soc. Trans.*, **42**, 412 (1923).

³ *Chem. Soc. Trans.*, **123**, 725 (1923).

CHAPTER XII

Preparation and Resolution of Inorganic Complex Salts

The importance of practical work need not be discussed here but it can be pointed out that one's knowledge of the complex salt is necessarily very superficial unless one carries out a few preparation and attempts some resolutions.

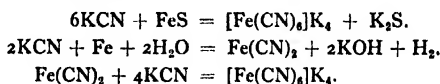
In the sequel, the preparation of some of the complex salts is given. They have been chosen on account of their importance, and also because their preparation is typical for this class of compounds. Some reactions are also given which involve a replacement of the components of the co-ordinated complex. No example is yet known of the direct replacement of the central metallic atom by another metal.

Two examples of resolutions are given, the one involving the use of an active acid, and the other the use of an active base. Resolutions of other compounds can be carried out in the same way, but it must be pointed out that this is by no means an easy process. Choice of the active acid or base is of great importance, as has already been pointed out. Then again the complex salts are frequently derivatives of very weak acids or bases, so that measures have to be taken to prevent hydrolysis. Research workers in this field must study very carefully the resolutions which have been already carried out, these being given fully in chemical literature.

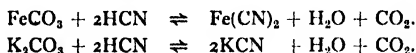
Potassium Ferrocyanide, $[\text{Fe}(\text{CN})_6]\text{K}_3$

Potassium ferrocyanide is generally known as yellow prussiate of potash.* It is manufactured commercially, two processes being employed.

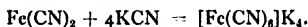
In the first, nitrogenous refuse¹ (blood, horns, leather scraps, &c.) is charred, and the black mass ignited with potash and iron filings. After cooling, hot water is added and the mixture filtered. The filtrate on evaporation gives yellow crystals of potassium ferrocyanide with the empirical composition $[\text{Fe}(\text{CN})_6]\text{K}_4 + 3\text{H}_2\text{O}$. This complex salt is not formed until the ignited mass is treated with water, for the yellow prussiate is decomposed by heat and cannot therefore be present in the ignited mass. The latter probably contains potassium cyanide, iron, and iron sulphide (sulphur being always present in animal refuse). These substances interact according to the following equations:



The second method is employed in illuminating gas factories,² for the gas contains a little cyanogen and hydrocyanic acid. After being freed from tar and ammonia, the gas is passed through purifiers which contain a solution of potash in which ferrous carbonate is suspended. The following reactions take place:



These reactions are reversible, but the products are immediately removed, forming the ferrocyanide



The ferrocyanide is extracted from the mass by means of its soluble calcium salt, this being then converted into the potassium salt by means of potassium carbonate.

Potassium Ferricyanide, $[\text{Fe}(\text{CN})_6]\text{K}_3$

If an aqueous solution of potassium ferrocyanide be treated with oxidizing agents such as chlorine, bromine, hydrogen peroxide, potassium permanganate, &c., it acquires a dark reddish colour due to the formation of the ferricyanide commonly known as red prussiate of potash. The preparation of this latter salt is best carried out by the following method, due to Walker.³

¹ Liebig, *Ann.*, 38, 215.

² Zimmermann, *Ber.*, 17, 243.

³ *J. A. C. S.*, 17, 68 (1895).

PREPARATION AND RESOLUTION OF SALTS 113

26 gm. of potassium ferrocyanide are dissolved in 200 c. c. of cold water, and 8 c. c. of concentrated hydrochloric acid added. To this mixture is added gradually a cold solution of 2 gm. of potassium permanganate in 300 c. c. of water. The oxidation is complete when a drop of the liquid gives only a brown coloration with a drop of ferric chloride. The excess of acid is then neutralized with potassium or barium carbonate, the solution filtered and the filtrate concentrated on the water bath, and then crystallized. The first fraction consists of the pure ferricyanide, the remainder is separated from the chlorides by fractional crystallization.

Properties. Dark red, rhombic prisms. Easily soluble in water. The solubility in water at different temperatures varies as follows:

Temperature: 4.4° C. 10° C. 15.6° C. 37.8° C. 100° C. 104.4° C.

Soluble in: 3.03 2.73 2.54 1.70 1.29 1.21 parts water.

Sodium Nitroprusside, $[\text{Fe}(\text{CN})_5(\text{NO})]\text{Na}_2 + 2\text{H}_2\text{O}$

Rust¹ recommends the following method.

40 gm. of potassium ferrocyanide are dissolved in 60 c. c. distilled water contained in a 500 c. c. beaker. 64 c. c. of nitric acid (S.G. 1.24) are added to this solution and the mixture is gently warmed on the water bath until the reaction is complete. The end point is ascertained by taking a few drops of the brown solution in a test tube and adding a few drops of a ferrous salt; a green but no blue precipitate should be formed. During the reaction, cyanogen, hydrogen cyanide, carbon dioxide and nitrogen are evolved. The mixture is allowed to stand for a few days, and is then neutralized with sodium hydroxide; excess should be carefully avoided. The neutral solution is heated to boiling, filtered, and concentrated by evaporation over a free flame. It is then allowed to cool, and an equal volume of alcohol added. This causes the precipitation of most of the potassium nitrate. The filtrate is then heated to drive away the alcohol, and from the dark red concentrated solution crystals separate; these are washed with a small amount of cold water. On concentration, the mother liquor will yield more of the product.

Properties. Ruby-red, transparent crystals. Soluble in 2.5 parts of cold water, also soluble in alcohol.

¹ Auleit. z. Darst. anorg. Präp (1907).

Sodium Cobalti-nitrite, $[\text{Co}(\text{NO}_2)_6]\text{Na}_3$

The following method is recommended by Billmann.¹

156 gm. of sodium nitrite are dissolved in 150 c. c. of hot water; after cooling to 40°–50° C. (the temperature of saturation), 50 gm. of cobalt nitrate crystals are added. To this mixture are added gradually 50 c. c. of 50 per cent acetic acid, the mixture being continuously stirred. A strong current of air is then passed through the solution for about thirty minutes. A small amount of precipitate separates; this consists of potassium cobalti-nitrite (sodium nitrite generally contains a small amount of the potassium salt). To the clear filtrate are added 250 c. c. of 96 per cent alcohol; this should be added gradually, as, otherwise, the precipitate separates out in a very finely divided state. The liquid is then filtered and the precipitate washed four times with 25 c. c. alcohol and twice with 25 c. c. ether, and dried in the air. Yield, 50–53 gm. This product generally contains a little of the potassium salt, from which it can be purified by extraction with water, in which the latter salt is but very sparingly soluble. The sodium salt is then again obtained from the solution by the addition of alcohol.

Properties. Yellow powder. Easily soluble in water. The concentrated solution is an analytical reagent for potassium, for which purpose it is best prepared as follows. 112 gm. of crystallized cobalt sulphate are dissolved in 500 c. c. water, 180 gm. sodium nitrite in 300 c. c. water, and 20 c. c. acetic acid in 50 c. c. water; the acetic acid solution is gradually added to the mixture. This is allowed to stand for several hours at 30°–40° C. and then cooled to 0° C. It is filtered from the separated sodium sulphate and the filtrate made up to 1 litre.

Chloro-pentammine-Cobaltic Chloride, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

This is prepared according to Sørensen² by the following method. 20 gm. of cobalt carbonate are dissolved in the minimum amount of 50 per cent hydrochloric acid, the solution is filtered, cooled and added to a mixture of 250 c. c. concentrated ammonia and 50 gm. of ammonium carbonate in 250 c. c. water. This mixture is then oxidized by the passage of a strong current of air for about three hours. To the oxidized mixture is added 150 gm. of air

¹ *Zeit. a. anal. Chem.*, 39, 286 (1900).

² *Zeit. anorg. Chem.*, 5, 369 (1894).

monium chloride, and the mass is placed in a porcelain dish and concentrated for a few hours on the water bath. Dilute hydrochloric acid is then added until the mixture is faintly acid. When the evolution of carbon dioxide has ceased, ammonia is added and the mixture shaken in a flask. Heating for an hour on the water bath ensures the complete disappearance of any tetrammine salt. After the addition of 300 c. c. concentrated hydrochloric acid, warming on the water bath for about forty minutes, and cooling, crystals of the pentammine salt separate. The product can be purified by warming it with 500 c. c. 2 per cent ammonia water, filtering from the little cobalt oxide formed, and then precipitating with concentrated hydrochloric acid. Yield, 30 gm.

Properties. Ruby-red, rhombic crystals. Soluble in water, insoluble in hydrochloric acid. An aqueous solution is decomposed on boiling.

Nitro-pentammine-Cobaltic Chloride, $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}$

Jørgensen¹ prepared this compound from the chloro-pentammine. 20 gm. of the latter are dissolved in a mixture of 200 c. c. water and 50 c. c. of 10 per cent ammonia. The small amount of cobalt oxide formed is separated by filtration. The mixture is cooled and made faintly acid by the addition of dilute hydrochloric acid. 25 gm. of sodium nitrite are then added and the mixture is heated on the water bath until the red precipitate first formed completely redissolves. 250 c. c. of concentrated hydrochloric acid are then added and the mixture well cooled, when brownish crystals separate. These are washed with alcohol and dried in the air.

Properties. Large yellowish brown crystals. Easily soluble in hot water, sparingly soluble in the cold.

Nitrito-pentammine-Cobaltic Chloride, $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$

This nitrito complex is isomeric with the nitro complex, whose preparation has been given in the preceding section. Jørgensen² gives the following method for the preparation of the nitrito compound.

10 gm. of chloro-pentammine-cobaltic chloride are dissolved in 150 c. c. of water and 25 c. c. of 25 per cent ammonia by gently warming the mixture. Traces of cobaltic oxide which may be

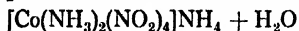
¹ *Zeit. anorg. Chem.*, 17, 463 (1898).
(D 340)

² *Zeit. anorg. Chem.*, 5, 168 (1894).
822

formed are separated by filtration, and the filtrate is neutralized with dilute hydrochloric acid. 10 gm. of crystallized sodium nitrate are then added; after these have gone into solution 10 c. c. of hydrochloric acid (1:1) are added. The precipitate which is gradually formed is filtered, and washed with cold water and alcohol.

Properties. Carmine-red, crystalline powder. The compound gradually changes into the isomeric nitro complex. This change takes place rapidly if a 10 per cent solution of the nitrito complex is mixed with an equal volume of concentrated hydrochloric acid.

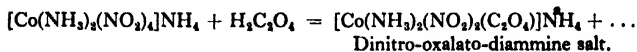
Preparation of Erdmann's Salt,¹



100 gm. of ammonium chloride and 135 gm. of sodium nitrite are dissolved together in 750 c. c. of water, and 25 c. c. of 20 per cent ammonia solution added. Into this mixture is poured a solution of 90 gm. of crystallized cobalt chloride in 250 c. c. of water, and the whole oxidized by passing a rapid current of air through the solution. This is then allowed to stand for five days in a porcelain basin, when a crop of crystals will have separated. The solution is filtered and the crystals are washed with cold water. The tetranitro-diammine complex is mixed with a yellow sparingly soluble polynuclear complex of cobalt; a separation can, however, be effected by shaking the mixture with lukewarm water, when the former dissolves. The dark brown solution is allowed to stand, and crystals of Erdmann's salt separate.

Properties. Large dark brown rhombic crystals. Sparingly soluble in cold water, more readily in warm water.

By treating 10 gm. of the above complex in 100 c. c. warm water with 10 gm. of crystallized oxalic acid in 50 c. c. water, at 50° C., oxides of nitrogen are evolved. The solution on standing deposits large crystals of a complex salt in which two of the above nitro groups are replaced by an oxalato group.²



Estimation of Cobalt in Erdmann's Salt.—It is first necessary to destroy the complex. This is best done by heating a solution of the complex with a solution of sodium hydroxide. The

¹ Jörgensen, *ZÄt. anorg. Chem.*, 17, 476 (1898).

² Jörgensen, *Zeit. anorg. Chem.*, 11, 440 (1896).

PREPARATION AND RESOLUTION OF SALTS 117

cobalt hydroxide precipitated is dissolved in dilute sulphuric acid. The solution is then neutralized with ammonia. To this neutral solution is added a neutral solution of sodium ammonium phosphate (containing about ten times as much of the salt as there is cobalt to be precipitated); a blue amorphous precipitate of cobaltous ammonium phosphate is produced. This is then boiled for about forty minutes, and the precipitate changes to a beautiful carmine-red crystalline precipitate of the same compound. The solution is filtered through a Gooch crucible, and the precipitate can either be dried at 105° C. and weighed as cobaltous ammonium phosphate, $\text{Co}(\text{NH}_4)\text{PO}_4$, or ignited and weighed as the pyrophosphate, $\text{Co}_2\text{P}_2\text{O}_7$.

Preparation and Resolution of Potassium Cobalt-oxalate, $\text{Co}(\text{C}_2\text{O}_4)_2\text{K}_3$

Preparation.¹—A mixture of 25 gm. of freshly precipitated cobalt carbonate, 250 c. c. of a saturated solution of potassium oxalate, and 230 c. c. of a saturated solution of oxalic acid is heated on the water bath and continuously stirred until all the carbonate has gone into solution. The solution is cooled to 40° C. and 30 gm. of finely divided lead peroxide are added. 50 c. c. of a 50% solution of acetic acid is then added very gradually, the mixture being well cooled and stirred during the addition. The dark green liquid is filtered and the complex precipitated from the solution by the addition of 400 c. c. of 96 per cent alcohol. The dark green potassium cobalt-oxalate is well washed with absolute alcohol and ether. Yield, 80 gm.

Properties. Dark green triclinic crystals. Readily soluble in water, insoluble in alcohol. An aqueous solution is very unstable; especially on exposure to light it decomposes, giving the cobalto-complex $[\text{Co}(\text{C}_2\text{O}_4)_2]\text{K}_2$.

Resolution.—This complex can be resolved by spontaneous crystallization² (cf. Chapter V). The crystallization must be carried out above 13.2° C., which is the transition temperature.

It can also be resolved by combination with an active base.³ A solution of the complex salt is mixed with a solution containing the equivalent amount of strychnine sulphate, and the mixture subjected to the process of fractional crystallization. The first fractions are found to consist of the strychnine salt of the *lævo* component. This salt is shaken up with a concentrated solution of

Jaeger and Thomas, *Proceed. Kon. Akad. v. Wet.*, 21, 1 (1918).

² Werner, *Ber.*, 45, 865 (1912).

potassium iodide, when sparingly soluble strychnine iodide separates. This is filtered, and the filtrate, which consists of a concentrated solution of the potassium salt of the *lævo* complex is mixed with 97 per cent alcohol, when the active salt is precipitated. Further fractions are treated in the same way; the last fractions are found to consist of the strychnine salt of the *dextro* complex.

Resolution of Triethylenediamine-Chromic Iodide, $[\text{Cr}(\text{en})_3]\text{I}_3$

6 gm. of the racemic salt are dissolved in 20 c. c. water, and a solution of 6 gm. of the sodium salt of nitrocamphor in 15 c. c. water added. A pale yellowish precipitate of dextrotriethylenediamine chromic salt of nitrocamphor separates. This is filtered and 2 gm. of nitrocamphor are added to the filtrate, when more of the above active salt separates. The precipitate is well washed with alcohol and ether, and then mixed with finely powdered sodium iodide, some water added, and the dark yellow liquid filtered. The precipitate is found to be *d*-triethylenediamine-chromic iodide; it is purified by dissolving it in the smallest amount of water, and precipitating it by means of sodium iodide. The *lævo* component can be obtained from the later fractions in the same way.

NAME INDEX

- Abegg, 2, 4.
 ● Abegg and Bodlander, 104.
 Avogadro, 1.
 •
 Bain, Mills and, 51.
 Baudisch, 95.
 Berzelius, 1.
 Billmann, 114.
 Blitz, 87.
 Blomstrand, 3, 6, 108.
 Bodlander, 88.
 Bodlander, Abegg and, 104.
 Bodlander and Fittig, 89.
 Bohr, 5.
 Braun, 44.
 Bredig and Walton, 11, 79.
 Caven and Ferguson, 85.
 Challenger, Kipping and, 49.
 Cleve, 45.
 Couper, 2.
 Cutter, Lowry and, 68.
 Dalton, 1.
 Dammer, 78.
 Dawson, 93.
 Dede, 96.
 Drude, 68.
 Dumas, 1.
 Ephraim, 86, 87.
 Erdmann, 33, 36, 53.
 Euler, 94, 101.
 Ferguson, Caven and, 85.
 Findlay, 59, 60.
 Fischer and Platau, 49.
 Fittig, Bodlander and, 89.
 Flatau, Fischer and, 49.
 Forsall, Locke and, 93.
 Frankland, 2.
 Fraser, Thomas and, 74.
 Friend, 110.
 Gerhardt, 1.
 Gmelin Krut, 101.
 Grossmann and Hunseler, 101.
 Guye, 49.
 Hantzsch, 51.
 Hittorf, 19, 87.
 Hofmann, 34.
 Hunseler, Grossmann and, 101.
 Hüttig, 83, 101.
 Humphrey, Werner and, 39.
 Jaeger, 64, 66, 68, 74, 75.
 Jaeger and Thomas, 59, 117.
 Jones, 49.
 Jørgensen, 6, 39, 43, 44, 45, 46, 96, 109, 115, 116.
 Kekulé, 2.
 Kipping, 49.
 Klein, Werner and, 39.
 Knight and Rich, 78.
 Kolbe, 2.
 Langmuir, 8.
 Le Bel, 4, 48, 49, 72.
 Lewis, 5.
 Ley and Winkler, 42.
 Lichtenstadt, Meisenheimer and, 49.
 Liebig, 1.
 Locke and Forsall, 93.
 Lowry, 68, 95, 110.
 Lowry and Cutter, 68.
 Manchot, 101.
 Maquenne, 50.
 Maruki, Shibati and, 53.
 Meisenheimer and Lichtenstadt, 49.
 Mills and Bain, 51.
 Mills and Nodder, 51.
 Miolati, 103.
 Nef, 3.
 Neville, Pope and, 49.
 Nodder, Mills and, 51.
 Ostwald, 87.
 Pasteur, 47, 57, 61, 63, 74, 75.
 Peachey, Pope and, 49, 74.
 Perkin, Pope, and Wallach, 51.
 Peyrone, 77, 78.
 Pope, 49, 52.
 Pope and Neville, 49.
 Pope and Peachey, 49, 74.
 Pope, Perkin, and Wallach, 51.
 Ramsay, 85.
 Reiset, 76, 78.
 Rich, Knight and, 78.
 Rideal and Thomas, 73.
 Roloff, 17, 18.
 Romijn, 96.
 Rust, 113.
 Rutherford, 5.
 Scacchi, 57.
 Sherril, 97.
 Shibati and Maruki, 53. •
 Sidgwick, 110.
 Sørensen, 110.
 Swarts, 49.
 Tassaert, 108.
 Thomas, 53, 62, 73, 75, 107.
 Thomas and Fraser, 74.
 Thomas, Jaeger and, 59, 117.
 Thomas, Rideal and, 73.
 Thomson, 4.
 Tschuganoff, 95.
 Van't Hoff, 2, 48, 49, 57, 72.
 Vernon, 82.
 Walden, 70.
 Walker, 112.
 Wallach, Pope, Perkin and, 51.
 Walton, Bredig and, 11, 79.
 Wedekind, 49.
 Werner, 5-10, 21, 24, 26, 27, 42, 51, 54-6, 61, 62, 68-70, 73, 81, 102, 103, 109, 117.
 Werner and Humphrey, 39.
 Werner and Klein, 39.
 Winkler, Ley and, 42.
 Zimmermann, 112. •

SUBJECT INDEX

- Affinity, residual, 8.
 Analysis of complex salts, 96.
 Anomalous rotation, 64.
 Asymmetric carbon atom, 48.
 Asymmetric molecules, symmetry of, 50.
 Asymmetry, molecular, 47.
 Basic salts, 102.
n-Benzil dioxime as a reagent for nickel, 95.
 Benzophenone tetracarboxylic acid, oxime of, 51.
 Binary compounds, 6.
 Cesium and rubidium, separation of, 94.
 Chlorides, bromides, and iodides, separation of, 94.
 Chloro-pentammine-cobaltic chloride, preparation of, 114.
 Chromic chloride, hexahydrates of, 28.
 Cobalt and nickel, separation of, 94.
 Cobalt, estimation in Erdmann's salt, 116.
 Cobalt, estimation of, 96.
 Cobalti-nitrite, preparation of sodium, 114.
 Cobalti-oxalat^o, preparation and resolution of potassium, 117.
 Complex ions, detection of the formation of, 12.
 Complex salts with co-ordination number equal to four, configuration of, 80.
 Complex salts with co-ordination number equal to four, types, 76.
 Complex salts with co-ordination number equal to six, configuration of, 39.
 Complex salts with co-ordination number equal to six, types, 21.
 Concentration cells, 89.
 Copper and cadmium, separation of, 93.
 Copper, titration with iodine in the presence of ferric iron, 96.
 Cupferron, 95.
 Diacido-diammine group, 78.
 Diacido-tetrammine group, 30.
n-Dimethylglyoxime as a reagent for nickel, 95.
 Dissociation of the amines on heating, 84.
 Distribution co-efficient, 17.
 Double salts, 87.
 Electromotive force, application of, in the study of complex salts, 19, 89.
 Erdmann's salt, constitution of, 33.
 Erdmann's salt, estimation of cobalt in, 116.
 Erdmann's salt, preparation of, 116.
 Erdmann's salt, structure of, 53.
 Ferricyanide, potassium, analysis of, 96.
 Ferricyanide, potassium, preparation of, 112.
 Ferrocyanide, potassium, preparation of, 111.
 Fluoro-chloro-bromo-acetic acid, 49.
 Hexacido group, 35.
 Hexammine group, 21.
 Hydrates, 25.
 Hydrates of chromic chloride, 28.
 Hydration, 32.
 Hydrogen peroxide, decomposition by the iodide ion, 11, 79.
 Inner complex salts, 33.
 Inositols, 50.
 Ionic migration and complex ions, 18.
 Ionization isomerism, 45.
 Isomerism of complex salts with co-ordination number equal to four, 80.
 Isomerism of complex salts with co-ordination number equal to six, 40.
 Isomerism, co-ordination, 44.
 Isomerism, hydration, 45.
 Isomerism, ionization, 44.
 Isomerism, optical, 51.
 Isomerism, structure, 43.
 1-Methyl-cyclohexylidene-4-acetic acid, 51.
 Molecular asymmetry, 47.
 Monacido-pentammine group, 26.
 Monacido-triammine group, 77.
 Nickel, estimation by means of *n*-benzil dioxime, 95.
 Nickel, estimation by means of *n*-dimethyl glyoxime, 95.
 Nitro-pentammine-cobaltic chloride, preparation of, 115.
 Nitro-pentammine-cobaltic chloride, preparation of, 115.
 Nitroprusside of sodium, preparation of, 114.
 Optical activity, 47.
 Optical activity and configuration of complex salts, 69.
 Optical activity and constitution of complex salts, 53.
 Optical activity and crystalline form, 74.
 Optical activity, cause of, 49.
 Optical activity, influence of the central atom on the magnitude of, 68.
 Optical activity of carbon compounds, 47.

- Optical activity of nitrogen, sulphur, selenium, tin, silicon, and phosphorus compounds, 49.
 Oximino cyclohexane carboxylic acid, 51.
- Pentacido-triammine group, 34.
 Phase rule, application in the study of complex salts, 20, 84.
 Poly-acids, 103.
 Polymeriam, 46.
 Polynuclear compounds, 54.
 Potassium cobalti-oxalate, preparation and resolution of, 117.
 Potassium, detection of, 94.
 Potassium ferricyanide, analysis of, 96.
 Potassium ferricyanide, preparation of, 112.
 Potassium ferrocyanide, preparation of, 111.
 Precipitation method of measuring the stability of complex salts, 88.
 Propylenediamine cobalti-chloride, isomers of, 56.
 Propyl-isopropyl cyan-acetic acid, 49.
- Qualitative analysis, application of complex salts, 92.
 Quantitative analysis, application of complex salts, 95.
- Racemisation, 72.
- Resolution of racemates into optically active antipodes, 57.
 Rotation, anomalous, 64.
 Rotatory power and constitution, 68.
- Sodium nitroprusside, preparation of, 113.
 Spatial arrangement of groups in the complex, 37, 80.
 Stability of complex salts, 83.
 Stability of complex salts, factors influencing the, 104.
 Stability of complex salts, measurement of the, 88.
 Structural isomerism, 43.
 Symmetry of asymmetric molecules, 50.
- Tetracido group, 79.
 Tetracido-diammine group, 33.
 Tetracido-triammine group, 32.
 Triacido-triammine cobalt, polymers of, 40.
 Triethylenediamine-chromic iodide, resolution of, 118.
- Valency, auxiliary and principal, 8.
 Valency, primary, 8.
 Valency, theories of, 1.
- Water of crystallization, 5, 104.

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